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**Electronic and local atomic structure of
iron-bearing minerals and glasses at
conditions of the Earth's mantle**

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Kurzfassung

Diese Arbeit untersucht das Struktur- und Elektronenverhalten von Eisen unter Hochdruckbedingungen des unteren Erdmantels anhand von Experimenten an Fe_2O_3 und eisenhaltigen haplobasaltischen Gläsern. Mittels Röntgenemissionsspektroskopie, resonanter Röntgenemissionsspektroskopie, Röntgendiffraktion und Synchrotron-Mössbauer-Spektroskopie werden Änderungen von Spin-Zustand, Valenz und lokaler Koordination bestimmt. Für Fe_2O_3 zeigt sich, dass die Entwicklung des Spin-Zustands eng mit strukturellen Phasenumwandlungen verknüpft ist. Ein ausgedehnter Bereich von gemischtem Spinzustand bei mittleren Drücken steht im Zusammenhang mit gemischtvalenten Phasen wie Fe_5O_7 . Bei höheren Drücken und Temperaturen bildet sich die Phase $\text{Fe}_{25}\text{O}_{32}$, wobei das Elektronenverhalten durch das Nebeneinander von Fe^{2+} und Fe^{3+} in unterschiedlichen Koordinationsumgebungen bestimmt wird. Der Spinzustand wird somit primär durch die Kristallstruktur kontrolliert. In haplobasaltischen Gläsern reagiert Eisen gradueller auf Kompression. Zweiwertiges Eisen zeigt deutliche Änderungen der lokalen Koordination, während dreiwertiges Eisen strukturell stabiler bleibt. Diese Entwicklung wird durch lokale strukturelle Umverteilungen bestimmt. Insgesamt wird das Verhalten von Eisen im unteren Erdmantel durch das Zusammenspiel von elektronischem Zustand, Struktur und Phasenbeziehungen kontrolliert, was entscheidend ist für die physikalischen und chemischen Eigenschaften eisenhaltiger Materialien im tiefen Erdinneren.

Abstract

This study investigates the structural and electronic behavior of iron under high-pressure conditions relevant to the Earth's lower mantle, combining experiments on Fe_2O_3 and iron-bearing haplobasaltic glasses. X-ray emission and resonant X-ray emission spectroscopy, X-ray diffraction, and synchrotron Mössbauer spectroscopy are used to constrain changes in spin state, valence, and local coordination. In Fe_2O_3 , spin-state evolution is closely linked to structural phase transformations. An extended mixed-spin regime occurs at intermediate pressures and is associated with mixed-valence oxides such as Fe_5O_7 . At higher pressures and temperatures, $\text{Fe}_{25}\text{O}_{32}$ forms, with electronic behavior governed by coexisting ferrous and ferric iron in distinct coordination environments. Thus, the spin is primarily governed by the crystal structure. In haplobasaltic glasses, iron responds more gradually to compression. Ferrous iron undergoes significant coordination changes, whereas ferric iron remains structurally more stable. These changes reflect local structural redistribution. Overall, the behavior of iron under lower mantle conditions is governed by the interplay of electronic state, structure, and phase relations, with important implications for the physical and chemical properties of deep Earth materials.

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1 Introduction

Although iron constitutes only a minor fraction of the lower mantle by volume, its oxidation state, coordination environment, and electronic configuration exert a major influence on the physical and chemical properties of Earth's deep interior, making Fe-bearing materials central to understanding lower mantle processes [1–4]. The behavior of iron under lower mantle conditions is fundamental to understanding the redox state, structure, and dynamics of Earth's deep interior. Iron exhibits a high degree of flexibility in both valence and crystal chemistry, allowing it to form a wide range of oxides and to adopt multiple structural roles in silicate melts [1, 4–8]. At pressures up to 800,000 bar and temperatures above 2000 °C [9, 10], this versatility becomes particularly pronounced. Under such conditions, Fe_2O_3 can transform into more complex iron oxides, such as Fe_5O_7 and $\text{Fe}_{25}\text{O}_{32}$, in which both ferric and ferrous iron are incorporated [11, 12]. In parallel, iron in silicate systems participates in melt structure as both Fe^{2+} and Fe^{3+} [13–15]. Investigating these complementary behaviors is essential for constraining how iron responds to extreme conditions in the lower mantle.

Experimental studies on initial $\alpha\text{-Fe}_2\text{O}_3$ at high pressure and high temperature demonstrate that iron oxides exhibit complex phase behavior, including the formation of higher-order oxides. These phases reflect changes in iron valence distribution, coordination environment, and electronic structure, highlighting the ability of iron to accommodate variable oxygen contents under compression. Such transformations provide direct insight into the redox properties of iron and the stability of oxidized phases under deep Earth conditions [11, 12].

At the same time, iron plays a central role in silicate melts, where its valence state and local coordination strongly influence melt structure and properties. In Fe-bearing basaltic compositions, ferric iron (Fe^{3+}) can act as a network-forming cation, contributing to the polymerization of the silicate framework, whereas ferrous iron (Fe^{2+}) is typically associated with network-modifying roles. The balance between these structural roles is expected to evolve with pressure, as compression alters coordination environments and electronic characteristics [6, 14–21].

Haplobasaltic glasses provide a simplified yet geochemically relevant system to investigate these effects. By reducing compositional complexity while retaining key features of basaltic melts, they enable systematic study of how iron speciation and structure respond to high pressures [2, 3, 22]. In combination with iron-bearing compositions, haplobasaltic glass systems allow direct comparison between the behavior of iron in oxide phases and in silicate melts, thereby linking redox processes across different chemical environments [4, 7].

In addition to structural changes, pressure also affects the electronic configuration of iron through spin-state transitions. Increasing crystal field splitting with compression can drive iron from high-spin toward low-spin-states, modifying its effective ionic radius and bonding behavior [1, 5, 23, 24]. These electronic changes are expected to influence

both the stability of iron oxides and the structural role of iron in melts. In the lower mantle, where pressures reach on the order of one million bar, such spin transitions may therefore play an important role in controlling phase relations, melt density, and element partitioning [1, 6, 25].

X-ray emission spectroscopy, particularly through analysis of the Fe $K\beta$ emission line, provides a powerful probe of the electronic state of iron under extreme conditions. Spectral features such as the $K\beta_{1,3}$ main peak and the $K\beta'$ satellite are sensitive to the number of unpaired electrons and thus to the spin-state [26]. Quantitative approaches, including the integral of absolute difference method and analysis of the first moment, allow tracking of subtle changes in spin-state as a function of pressure [27, 28].

In this study, Fe $K\beta$ X-ray emission spectroscopy is applied to both Fe_2O_3 at high pressure and temperature, and iron-bearing haplobasaltic glasses with varying ferric iron content at high pressure to investigate the electronic evolution of iron. For Fe_2O_3 , the method is combined with resonant X-ray emission spectroscopy, and structural changes are investigated using X-ray diffraction. The haplobasaltic glasses are studied using X-ray emission spectroscopy in combination with synchrotron Mössbauer spectroscopy for an in-depth insight into electronic and structural evolution.

By linking the formation of complex iron oxides with the behavior of iron in simplified basaltic melts, this study provides new insights into the redox and electronic flexibility of iron under lower mantle conditions. These results contribute to a more comprehensive understanding of how iron influences phase stability, melt structure, and the physical properties of deep Earth materials.

2 Earth structure, processes and iron in the lower mantle

Understanding the structure and dynamic evolution of Earth's interior requires detailed knowledge of the physical and chemical behavior of iron-bearing materials at high pressures and temperatures. Although iron (Fe) constitutes only a minor fraction of the lower mantle by volume, it exerts a disproportionate influence on its physical and chemical properties and is therefore essential for understanding deep Earth processes. [1–3]. Its oxidation state, coordination environment, and electronic configuration strongly influences seismic wave velocities, density, melting behavior, thermal and electrical partitioning, and redox cycles. As a consequence, constraining the high-pressure properties of Fe-bearing phases, such as Fe_2O_3 and (haplo-) basaltic compositions relevant for subducted oceanic crust, is central to interpreting geophysical observations and modeling deep mantle processes [1, 4–8].

The present chapter introduces the geophysical and geochemical context of the deep Earth, lays out the central role of iron in mantle processes, and motivates the study of Fe-bearing oxides and silicate glasses under lower mantle conditions. The layout of the chapter follows a logical progression from the large-scale structure of the Earth's interior to the microscopic electronic transitions in iron ions, and the specific experimental motivations for investigating haplobasaltic glasses at high pressure and Fe_2O_3 at high pressure and high temperature.

2.1 Structure and pressure-temperature conditions of the Earth's interior

Earth's internal structure is typically described as a layered system composed of the crust, upper mantle, transition zone, lower mantle, and core, with each region characterized by distinct mineralogical, seismic, and thermodynamic properties. The Preliminary Reference Earth Model (PREM) [9] provides radially averaged profiles of density, compressional and shear velocities, and elastic properties, and is the standard reference for interpreting seismic data. Starting from the surface, these layers are (cf. Fig. 2.1 left):

- **Crust (~0-35 km):** A thin silicate layer forming the continents and ocean basins [29].
- **Upper mantle (~35-400 km):** Composed primarily of olivine($(\text{Mg,Fe})_2\text{SiO}_4$)-rich assemblages [30]; characterized by increasing pressure and temperature with depth [10].
- **Transition zone (~400-660 km):** Defined by mineral phase transitions, which influence mantle convection patterns and control water storage [31].

- **Lower mantle (~660-2890 km):** Dominated by bridgmanite ((Mg,Fe)SiO₃) and ferropericlase ((Mg,Fe)O) [32]. This region is the focus of most deep-mantle mineral physics research.
- **Outer core (~2890-5150 km):** A liquid iron and nickel alloy [8] where convective motion generates the Earth's magnetic field [33].
- **Inner core (~5150-6371 km):** A solid Fe-Ni alloy [8] undergoing slow crystallization and anisotropic growth [34].

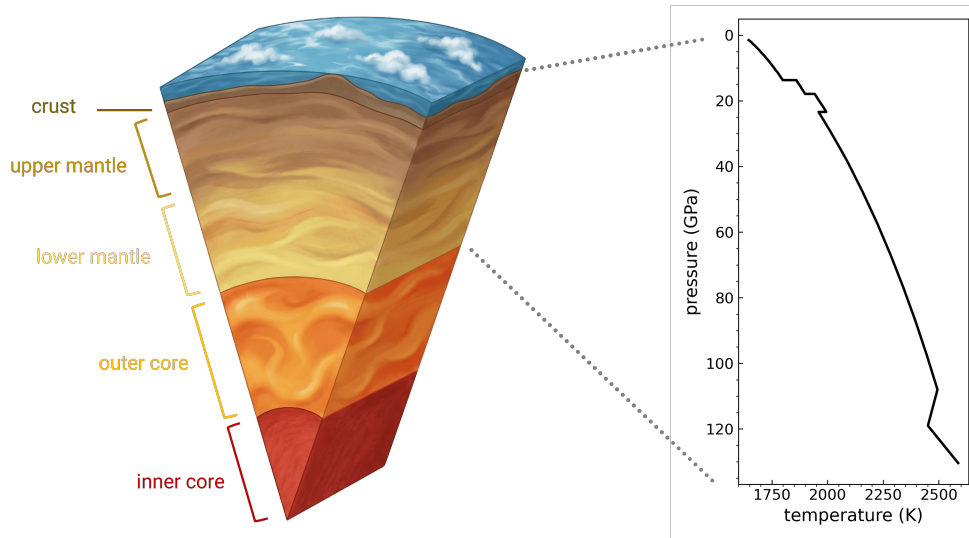


Figure 2.1: **Left)** Simplified depiction of the inner Earth's layers (improved with AI [35]). **Right)** A model of the Earth's adiabatic temperature profile from the crust through the lower mantle (after Katsura et al. [10]).

The pressure, temperature, and mineralogical composition across these layers determine how iron behaves structurally and electronically, forming the basis for the mantle processes discussed in this chapter.

This work will mostly focus on the lower mantle, a useful estimate of the pressure and temperature profile through the mantle is provided by the adiabatic temperature profile (cf. Fig. 2.1 right) [10]. The lower mantle extends from approximately 660 km to 2900 km depth, corresponding to pressures from about 24 GPa to 136 GPa. Recent refinements based on thermodynamic modeling of mantle minerals suggest temperatures of approximately 2000-2100 K at the top of the lower mantle, increasing to around 2600 K to 3500 K, depending on the model applied, near the core-mantle boundary. The precise course of the geotherm depends on thermal conductivity, radiative heat transfer, and the distribution of heat-producing elements [10, 36]. These thermodynamic conditions form the basis for evaluating the high-pressure behavior of iron-bearing oxides and melts discussed in the following sections.

The bulk silicate Earth (BSE), comprising the Earth's mantle and crust but excluding the core, is dominated by Mg-rich silicate and oxide phases, principally bridgmanite, ferropericlase, and Ca-perovskite. Although iron occurs only in modest concentrations, it strongly influences the physical and chemical properties of lower-mantle minerals [8, 32]. Iron constitutes only about 8 wt% when expressed as total iron reported as FeO [37],

though it strongly modifies compressibility, seismic velocities, viscosity and electrical conductivity [1, 5, 38]. Iron is also the primary carrier of variable oxidation states in the mantle, and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is a key parameter for controlling mantle redox conditions [4]. These characteristics underscore why iron-bearing materials must be examined under the relevant high pressure and high temperature (HP/HT) regime of the lower mantle.

2.2 Geochemical and geophysical role of iron

Iron plays a disproportionate role in governing the physical and chemical properties of the mantle, not because of its abundance, but because it is the principal element through which electronic, structural, and redox degrees of freedom are coupled [1]. Its capacity to adopt multiple oxidation states (Fe^{2+} (ferrous) and Fe^{3+} (ferric)), occupy different coordination environments, and undergo pressure-induced electronic spin transitions makes iron uniquely sensitive to changes in pressure and temperature [1, 5, 39]. As a result, variations in iron speciation affect transport properties in deep-Earth materials [1, 6]. Even small amounts of Fe substituting for Mg or other cations in bridgmanite or ferropericlase measurably alter their bulk moduli, influencing seismic wave speeds and the density structure of the mantle [5, 39].

Because redox reactions involving Fe^{2+} and Fe^{3+} regulate the oxygen fugacity of the mantle, iron plays a central role in determining mineral stability, melt structure, and the behavior of volatiles [4, 7]. High pressure shortens Fe-O bond lengths, strengthens ligand fields, and stabilizes low-spin states [1, 5, 39], while simultaneously pressure can influence Fe^{3+} stability in specific crystal structures via coupled substitutions and site energetics [1]. These effects reflect a balance of crystal-field stabilization, electron-pairing energies, and lattice enthalpy under compression [1, 5]. The microscopic mechanisms underlying these transitions are discussed in Chapter 3.1, and their macroscopic consequences are evident throughout the mantle [1, 5, 6, 39].

Changes in iron's electronic and structural state affect seismic velocities, rheology, and melt behavior [1, 5, 19]. Spin transitions modify volume and compressibility [1, 5]; valence changes influence melt polymerization, viscosity, and density [1, 19]; and coordination changes alter local bonding environments [1]. These factors collectively determine how melts rise or stall, how seismic waves propagate, and how chemical heterogeneities develop at depth [1, 5, 40]. The reduction in volume associated with the low-spin-state, for example, may contribute to seismic discontinuities or density contrasts that influence melt retention near the core-mantle-boundary (CMB) [1, 5, 19, 40]. In addition, pressure-induced changes in magnetic order, including the collapse of long-range antiferromagnetic alignment, reflect modifications in exchange interactions and can influence phase stability and thermodynamic properties under deep-mantle conditions [41]. Table 2.1 displays the influence of iron on the mantle's characteristic properties.

Seismic observations reveal velocity anomalies in the lowermost mantle that are commonly interpreted to reflect variations in iron distribution and speciation [6]. Ultra-low velocity zones (ULVZs) at the base of the lower mantle are characterized by reductions in seismic velocities of up to 30% and typical thicknesses of 10-15 km [42–44]. These anomalies are

Table 2.1: Influence of iron properties on geophysical and geochemical characteristics of the mantle, summarized from experimental, theoretical, and seismological studies [1, 4–7, 39].

iron-controlled variable	primary effect	geophysical consequence
oxidation state ($\text{Fe}^{2+}/\text{Fe}^{3+}$)	density, melt structure	melt buoyancy, phase stability, redox buffering
electronic spin-state	ionic radius, compressibility	seismic velocities, elastic anomalies, partitioning
coordination environment	bond strength, packing efficiency	density contrasts, viscosity variations
partitioning behavior	Fe distribution between phases	chemical heterogeneity, melt retention
electronic structure	charge mobility, absorption	electrical and radiative conductivity
magnetic order	exchange interactions, spin alignment	phase stability, magnetic collapse across transitions

consistent with the presence of iron-rich melts, melt-solid mixtures, or solid phases with elevated iron content, as suggested by high-pressure experimental and theoretical studies [6, 19]. In particular, pressure-induced changes in the electronic state of iron can modify melt density and stability, promoting the accumulation and retention of iron-rich melts near the CMB [19]. These seismic expressions therefore provide important constraints on the distribution and transport of iron in the lowermost mantle and link seismic observations to deep-mantle chemical and physical processes [6]. Beyond present-day mantle structure, iron-controlled density may also have played a fundamental role during earlier stages of Earth’s evolution.

During the early Earth, higher mantle temperatures and more extensive melting likely amplified the importance of iron-controlled melt buoyancy. Experimental studies show that iron enrichment increases melt density under deep-mantle conditions, potentially promoting gravitationally stable basal magma oceans or long-lived melt layers above the CMB [18, 45]. Under such conditions, variations in iron speciation and electronic state may have influenced whether melts ascended to form early crustal reservoirs or remained trapped at depth [19]. Consequently, iron likely played a key role in early chemical differentiation and the thermal evolution of the deep mantle.

Subduction delivers oxidized, iron-bearing materials into the deep mantle, further modifying redox conditions and contributing to the chemical complexity of lower-mantle reservoirs [4, 46]. Elevated $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios in subducted crust influence melting behavior and phase stability, potentially generating Fe-rich melts or solids that may contribute to ULVZ formation and other seismic anomalies [4, 47]. These processes highlight the central role of iron in shaping the physical and chemical landscape of the lower mantle [4, 46, 47].

Overall, iron’s redox flexibility, electronic variability, and structural adaptability make it fundamental to understanding deep-mantle dynamics [1, 4, 25, 47]. Its influence spans seismic wave propagation, melt generation, heat transport, redox evolution, and deep oxygen cycles [1, 18, 25, 47, 48]. This central importance motivates the high-pressure

investigations presented in this thesis and sets the stage for the theoretical framework introduced in the following chapter.

2.3 Deep mantle redox cycles and oxygen reservoirs

Redox processes in the deep mantle are fundamentally controlled by the speciation of iron [4]. As the dominant element capable of adopting multiple oxidation states, iron can cycle between Fe^{2+} and Fe^{3+} and thereby regulates the oxygen fugacity f_{O_2} , which describes the redox conditions of a system and the availability of oxygen for chemical reactions [4, 7]. Variations in f_{O_2} influence mineral stability, melting behavior, volatile speciation, and the formation of iron-rich melts or solid phases at depth [4, 7, 48].

Within this redox framework, ferric iron-bearing crystalline phases play a special role because they can store and release oxygen during structural or electronic transitions and decomposition at high pressure and temperature. In particular, high-pressure phase transitions in Fe_2O_3 involve changes in structural coordination and formation of higher oxides, which may be associated with the release of oxygen and the presence of mixed iron valence states [11, 49, 50]. The stability fields of these ferric phases are therefore directly linked to the prevailing oxygen fugacity, allowing Fe_2O_3 and related compounds to act as transient oxygen reservoirs in the deep mantle [11, 51]. Such processes provide essential geochemical context for the high-pressure behavior of Fe_2O_3 investigated in this thesis.

A complementary manifestation of deep-mantle redox processes is found in silicate melts and glasses, where iron commonly occurs in mixed valence states [13–15]. Pressure or temperature changes in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio modify local coordination environments, melt polymerization, and short-range structure, leading to measurable changes in spectroscopic signatures [14–16]. Understanding how iron valence evolves in these amorphous systems is therefore critical for interpreting their role as analogs for deep silicate melts and for assessing their contribution to redox-sensitive processes in the mantle [14, 15, 17]. Throughout this work, ‘glass’ refers to an amorphous silicate produced by quenching a melt.

2.4 Fe_2O_3 in the context of deep-mantle conditions

Fe_2O_3 represents the ferric endmember of iron oxides and is therefore a key reference material for understanding the behavior of Fe^{3+} in the deep mantle [11, 49]. Because ferric iron strongly influences redox equilibria, oxygen storage, and the stability of mantle phases, Fe_2O_3 plays an important role in the deep Earth [4, 11]. Its capacity to undergo changes in coordination and electronic configuration under conditions of the lower mantle makes it relevant for this thesis [11, 49].

Banded iron formations (BIFs) provide an additional geological context for the significance of Fe_2O_3 . These ancient sedimentary deposits, composed of alternating layers of iron-rich minerals (primarily hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4)) and silica (SiO_2), formed between 3.8 and 1.8 billion years ago constitute one of the largest known reservoirs of ferric iron at Earth’s surface [52]. Because Fe_2O_3 is a major component of BIFs, their

formation reflects large-scale oxidation of Fe^{2+} to Fe^{3+} and contributes to the long-term distribution of ferric iron within the Earth system [52]. Subduction of such Fe^{3+} -rich materials over geological time may provide a pathway for introducing oxidized iron into the mantle, linking surface redox processes with deep-mantle reservoirs [53].

At high pressures and temperatures, Fe^{3+} -bearing phases can act as carriers and participants in oxygen exchange, and transformations involving Fe_2O_3 may participate in redox cycling at depth [11, 48]. These processes influence density, elasticity, and transport properties and are therefore important for interpreting seismic and geodynamic observations, particularly in regions where iron-rich materials interact with surrounding mantle minerals or with metallic iron near the CMB [11, 48, 54].

In this thesis, Fe_2O_3 is used as a model system for investigating the behavior of ferric iron under lower mantle conditions. Its structural, electronic, and redox responses to compression provide a framework for linking spectroscopic signatures to changes in spin-state and coordination. A detailed examination of these aspects, including phase relations, electronic transitions, and comparisons to previous studies, is presented in Chapter 5 [11].

Understanding the high-pressure behavior of Fe^{3+} in crystalline phases such as Fe_2O_3 represents one side of the deep mantle redox framework. The complementary case involves iron in silicate melts, represented here by haplobasaltic compositions, which serve an important function in melt transport, redox cycling, and the physical properties of deep mantle reservoirs [18, 19, 54].

2.5 Haplobasaltic melts and glasses at high pressure

Basaltic materials are a major component of oceanic crust, primarily in the form of mid-ocean ridge basalt (MORB). MORB forms as solidified, (partially) crystallized rock from magmas erupted at mid-ocean ridges; depending on cooling history, the solidified rock may additionally contain a glassy component. As oceanic crust is transported into the mantle during subduction (cf. Fig. 2.2), it is not continuously molten — the basaltic rock remains predominantly solid and recrystallizes in response to the evolving pressure and temperature along the subduction path [55]. Renewed partial melting only occurs once the basalt solidus is locally exceeded, which requires comparatively unusual conditions (e.g., subduction of young, still-hot lithosphere) and is therefore a rare occurrence [56]. Where such melts do form, their physical properties (especially density, compressibility, melt behavior) strongly influence how they move and accumulate in the deep Earth [6, 18, 19]. Because iron is the main redox-active element in these compositions, understanding its coordination environment and oxidation state in the solid basaltic rock and any associated melt, is essential for describing melt behavior under lower-mantle conditions [6, 18–20].

At lower mantle pressures, basaltic melts experience large changes in density and compressibility. Experimental and computational studies indicate that melt densities may approach or exceed those of surrounding mantle minerals, leading to gravitational stagnation or accumulation of melt layers [18–20]. These density variations depend sensitively on melt structure, the coordination environment of network-forming cations,

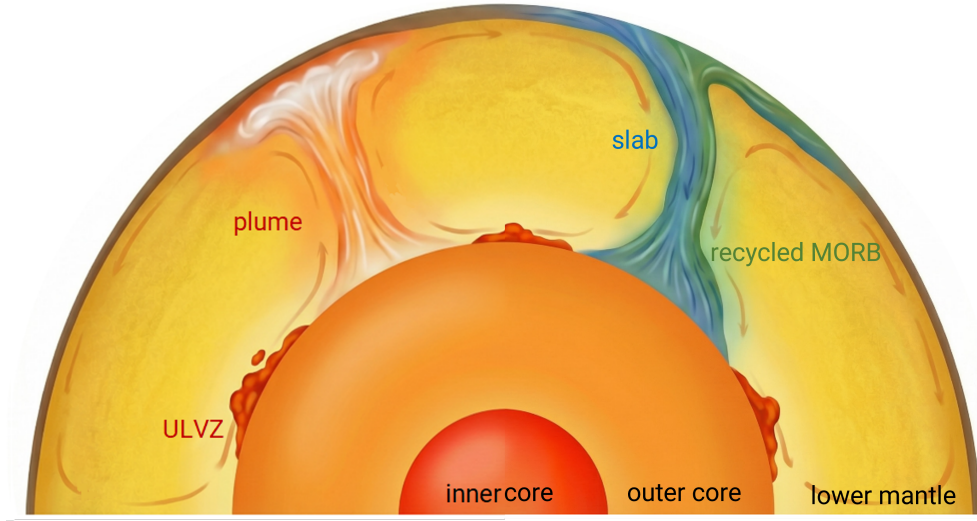
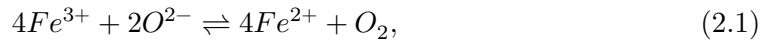


Figure 2.2: Schematic and simplified section of the lower mantle processes including ULVZ and plumes, which transport material upwards. Contrastingly, slab is subduction bringing, for example MORB, into the lower mantle (improved with AI [35])

and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. Variations in iron valence, therefore, exert control on melt buoyancy and the formation of iron-rich melt or ULVZ-like reservoirs at depth [18–20].

Recent work further demonstrates that melt-solid density contrasts at deep-mantle conditions cannot be explained by compressibility alone. The partitioning of Fe between melt and solid, and in particular the electronic spin-state of iron in the melt, wield a dominant control on melt density at lower-mantle and CMB pressures. A transition from high-spin to low-spin iron reduces the local volume and stabilizes more compact local environments in silicate melt, thereby increasing melt density and enhancing the tendency of iron-rich melts to become neutrally or negatively buoyant relative to surrounding bridgmanite- and ferropericlase-dominated assemblages [57].

The structural role of iron in silicate melts depends on both oxidation state and coordination [14, 15, 22]. In most basaltic compositions, ferrous iron behaves predominantly as a network modifier [13, 14], occupying higher coordination sites, breaking Si-O-Si linkages, and generating non-bridging oxygens (NBOs) [14]. This depolymerizes the melt, lowers viscosity, and increases compressibility [14, 18, 58]. Ferric iron can act either as a network modifier or as a network former, depending on its coordination environment [17, 22]. When Fe^{3+} is incorporated in tetrahedral coordination it enters the silicate framework as a network-forming cation and contributes to a more polymerized network with reduced NBO abundance, whereas octahedrally coordinated Fe^{3+} behaves structurally more like Fe^{2+} and depolymerizes the melt. These effects are linked through the redox equilibrium [59]:

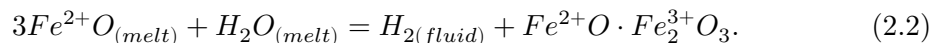


which couples melt polymerization directly to oxygen fugacity and Fe valence [3, 13, 14].

Polymerization-depolymerization reactions arise when changes in iron oxidation state or coordination modify the number of NBO in the melt. Increasing Fe^{2+} content, or

stabilizing Fe^{3+} in higher-coordination (modifier-like) sites, increases non-bridging oxygen per tetrahedra (NBO/T), depolymerizing the network and reducing viscosity, whereas the incorporation of tetrahedral Fe^{3+} as a network-forming species promotes a more polymerized structure [3].

Volatile effects on Fe oxidation are important because components such as H_2O and CO_2 change the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. Water typically increases Fe^{3+} concentrations through reactions such as



Since subducted crust contains hydrous and carbonated material, volatile-driven changes in Fe oxidation can strongly influence melt structure, density, and stability in the deep mantle [15, 60, 61].

Distribution of iron between melt and crystalline phases depends on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio and the coordination preferences of lower mantle minerals. Fe^{3+} partitions more strongly into bridgmanite, whereas Fe^{2+} has greater affinity for ferropericlasite [4, 62, 63]. These tendencies influence the evolving composition of both melt and solid phases, thereby affecting melt buoyancy and the likelihood that Fe-rich melts rise, sink, or remain trapped at depth, with possible implications for the formation of ULVZ [18, 19, 62, 63].

Iron and physical transport properties are closely linked because iron strongly influences optical absorption and electrical conductivity in both silicate melts and solid mantle phases. Changes in Fe valence or coordination modify the electronic absorption spectrum and thus radiative thermal conductivity in silicate melts and glasses [3], while variations in Fe^{3+} content or spin-state affect the electrical conductivity of lower-mantle minerals such as ferropericlasite [54]. These transport properties influence heat transfer in the lowermost mantle and play an important role in governing the heat flux across the CMB [54].

High-pressure behavior of basaltic melts influences whether melts become neutrally buoyant or denser than surrounding mantle minerals at depth [18, 19]. Dense, Fe-rich melts may form stable layers or lenses, providing one mechanism for ULVZ formation [18, 19]. Structural information preserved in high-pressure glasses quenched from such melts offer valuable constraints on Fe coordination and oxidation state as direct measurements of melts in the liquid state are difficult [19, 20].

Glasses as useful analogs follow from their ability to preserve the short-range atomic structure of the liquid state. Although glasses lack the dynamic properties of melts, their Fe coordination environments and redox-related structural features can, under appropriate quench conditions, remain representative of the melt at the moment of quench. This makes glasses powerful proxies for investigating melt structure at pressures [3, 22]. The motivation for studying basaltic compositions in particular follows from the fact that magmas generated by partial melting of the Earth's mantle have essentially this composition. In this thesis, high-pressure haplobasaltic glasses (HBGs), a simplified basalt composition of Ca, Mg, Si, Al, Fe and O, provide insight into Fe^{2+} - and Fe^{3+} -bearing environments relevant for deep mantle melt behavior. However, interpretation of glasses as melt equivalents must be taken with care, Wilke et al. [22] emphasize that the structure preserved in a glass reflects the configuration frozen in near the glass

transition temperature and may therefore differ from the structure of the melt at higher temperatures. XANES and EXAFS studies demonstrate that Fe coordination in melts differ from that observed in quenched glasses, with evidence for lower coordination and shorter Fe-O distances in the melt. Moreover, Mössbauer hyperfine parameters vary with quench rate. These observations imply that glass structures do not always faithfully represent melt configurations, particularly with respect to Fe coordination and local geometry [22]. Recent work by Shim et al. [57] has shown that cold-compressed glasses do not necessarily relax into melt-like local structures at high pressure, and can retain high-spin Fe fractions that are significantly larger than those in coexisting melts. These findings highlight that high-pressure glasses must be interpreted with care: they provide valuable constraints on local Fe environments, but may underestimate the extent of spin collapse in the corresponding melts. The spin-state of iron is dependable on local and not on long or intermediate range order, thus non-relaxed glasses may show different iron local order [57].

2.6 Concluding remarks

The behavior of iron under extreme pressure and temperature conditions governs many of the key physical processes operating in the deep mantle [1, 4, 7]. Variations in iron coordination, valence, and spin-state modify density, elasticity, and transport properties in both crystalline and melt phases, linking atomic scale electronic behavior to macroscopic phenomena such as seismic wave propagation, melt stability, and the formation of deep mantle anomalies including ULVZs [1, 5, 6]. These connections highlight the need to understand how microscopic electronic and structural transitions in iron translate into observable geophysical signatures.

Because geophysical observations and computational models alone cannot uniquely resolve iron's oxidation state, coordination environment, or spin configuration at relevant conditions, direct experimental constraints are essential [1, 5]. Spectroscopic methods applicable at high pressure and temperature conditions, such as X-ray spectroscopy, synchrotron Mössbauer spectroscopy (SMS), and X-ray Diffraction (XRD), provide the ability to detect spin transitions, quantify $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios, and determine crystal structure, respectively [27, 64, 65]. Studying Fe_2O_3 at deep Earth conditions constrains the behavior of ferric iron and its role in redox equilibria and oxygen storage [11], while investigations of HBG reveal the structural and electronic properties of melts derived from subducted oceanic crust [18, 19]. Together, these complementary systems help reconstruct iron driven processes that shape the physical and chemical evolution of the lower mantle.

Taken together, the behavior of Fe^{3+} -bearing crystalline phases such as Fe_2O_3 and the evolution of iron in basaltic melts define two complementary aspects of deep-mantle redox and structural processes. While Fe_2O_3 provides insight into the stability, coordination, and electronic behavior of ferric iron under compression [11, 49], iron-bearing melts and glasses capture the coupled effects of valence, coordination, and structural disorder relevant to partially molten regions of the mantle [3, 18, 19, 22]. Both systems highlight how changes in iron coordination, oxidation state, and spin configuration influence density, elasticity, transport properties, and ultimately the seismic signatures of the lower mantle [1, 4, 5]. These considerations motivate a closer examination of the electronic

and structural transitions of iron under extreme conditions, which form the focus of the next chapter.

To interpret these experimental observations, a theoretical framework is required. The following chapter introduces the electronic, structural, and crystal-field concepts necessary to describe how iron responds to compression and heating. This theoretical foundation enables a quantitative interpretation of the spectroscopic and diffraction fundamentals and results presented later in this thesis and provides the link between microscopic electronic structure and the macroscopic properties of materials in the deep Earth.

3 Theory

This chapter introduces the fundamental physical concepts required to describe the electronic and structural behavior of iron as a transition metal at high pressure and high temperature conditions. In particular, crystal field theory and pressure-induced spin transitions are discussed, as they form the basis for interpreting the experimental results presented in this thesis. In addition, the theoretical principles underlying the spectroscopic and diffraction methods used to probe iron-bearing materials are outlined, providing the framework for connecting measured spectra to microscopic electronic structure.

3.1 Electron spins states of iron and crystal field theory

Iron is a transition metal, characterized by partially filled $3d$ orbitals. This electronic configuration is central to its variable spin-states and underlies the pressure- and temperature-induced electronic transitions observed in iron-bearing minerals and glasses [23].

A fundamental framework for describing this electronic behavior is the crystal field theory (CFT), an electrostatic model that treats the interaction between a positively charged central metal ion and its surrounding ligands as a negative point charge. Although CFT neglects covalent orbital overlap between the metal and ligand, it provides a useful approximation for understanding spin-states and magnetic properties in iron-bearing systems [23, 24, 26, 66].

In an **octahedral coordination**, the five $3d$ orbitals of the transition metal split into two sets with different energies. The higher-energy e_g orbitals (d_{z^2} , $d_{x^2-y^2}$) are oriented along the Cartesian axes, while the lower-energy t_{2g} orbitals (d_{yz} , d_{xz} , d_{xy}) are located between these axes (Fig. 3.1). The energy difference between these two sets is referred to as the crystal field splitting energy (Δ_c or $10 Dq$). The electronic configuration of an isolated iron atom is $[\text{Ar}]3d^64s^2$. In iron-bearing oxides or glasses, the oxidation state and the resulting electronic configuration differ due to hybridization between iron and ligand orbitals [1, 23, 25].

In the following the electron configuration of the two oxidation states of ferrous (Fe^{2+} , $[\text{Ar}](3d^6)$) configuration and ferric (Fe^{3+} , $[\text{Ar}](3d^5)$) iron in an octahedral coordination will be showcased. Because of a greater distance of the t_{2g} orbitals to the ligand, they experience less repulsion and therefore are energetically more favorable. The six ligands are located on the Cartesian axes, just like the beforehand mentioned e_g orbitals, form the vertices of an octahedron. This ligand placement is the reason for the energy difference [1, 23].

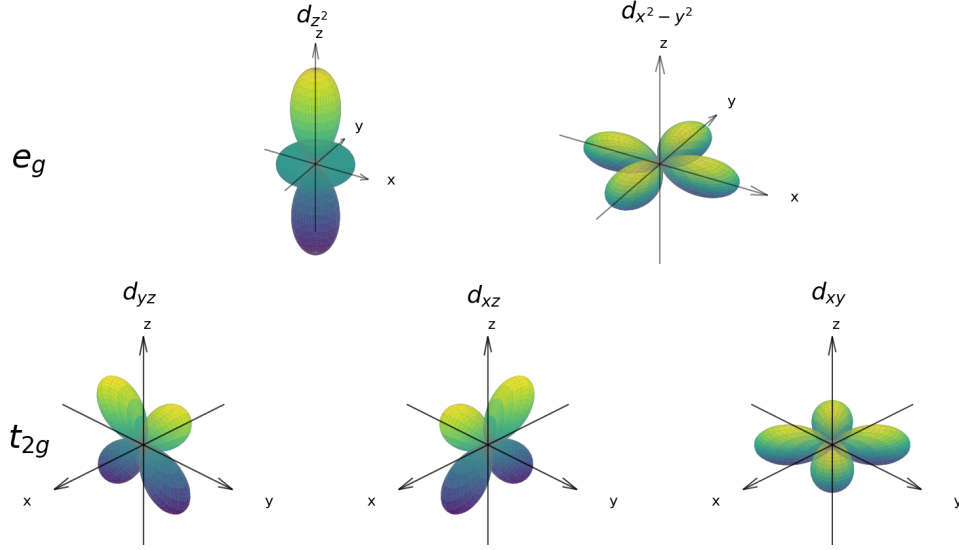


Figure 3.1: Depiction of 3d electron orbitals in an octahedral coordination (modified after Lin et al. [1]).

The electrons occupy individual orbitals according to Hund's rule, maintaining the same spin as long as the crystal field splitting energy is lower than the energy required for spin pairing. Spin pairing refers to the occupation of two electrons in the same orbital [23].

At ambient conditions, typical crystal field splitting energies for ferric iron in octahedral oxides as in Fe_2O_3 is $\approx 1.4 \text{ eV}$ [67]. When the metal-ligand bond length decreases, the crystal field splitting energy increases approximately with r^{-5} , where r denotes the Fe-O distance. As a result, it can become energetically favorable for electrons to pair within the lower-energy orbitals rather than occupy higher-energy orbitals with parallel spin. This competition between crystal field splitting energy and spin pairing energy gives rise to spin crossover transitions [1, 23, 68].

Such changes in crystal field strength may occur either continuously within an isostructural compression, where bond shortening enhances the ligand field without changing the crystallographic symmetry, or discontinuously across structural phase transitions that modify coordination geometry, symmetry, or polyhedral distortion. Both mechanisms are relevant in iron-bearing oxides and silicates under high-pressure and high-temperature conditions.

For the oxides and mineral used here, ferrous and ferric iron are at ambient conditions in the high-spin (HS) state with a spin of 2 and 2.5, respectively. In case of a spin crossover it results in a low-spin (LS) state with a spin of 0 and 0.5 for ferrous and ferric iron, respectively (cf. Fig. 3.2) [1, 23, 25, 68].

While octahedral coordination is dominant in many crystalline iron-bearing phases, iron can also occupy tetrahedral sites. In a **tetrahedral coordination**, the four ligands around the iron form a tetrahedron. Here, the e_g and t_{2g} designations are replaced by e and t_2 , respectively, as the tetrahedral environment lacks an inversion center. The ligands in this case are located between the Cartesian axes and therefore the d_{z^2} and $d_{x^2-y^2}$ orbitals, forming e , are energetically more favorable compared to the t_2 energy

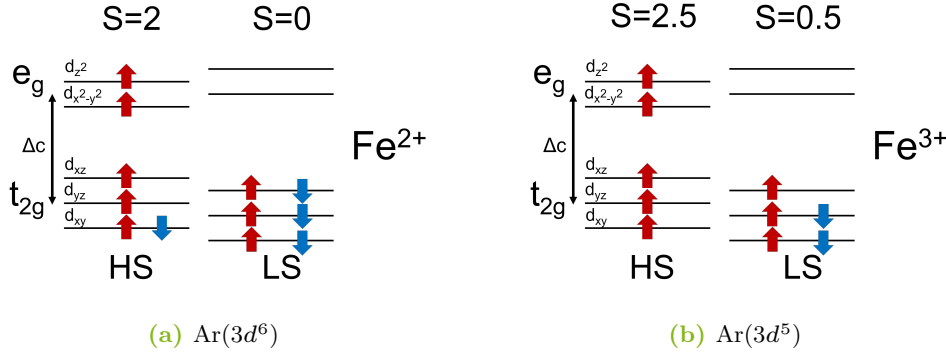


Figure 3.2: Orbital splitting and occupation in octahedral coordination with degenerated energy levels e_g and t_{2g} for HS and LS state for (a) ferrous iron and (b) ferric iron. The crystal field splitting energy is labeled as Δ_c (modified after Lin et al. [1]).

level, in contrast to the octahedral coordination. The crystal field splitting energy in tetrahedral coordination is smaller compared to the octahedral coordination [23, 24].

Under high pressure or temperature conditions, deviations from ideal coordination geometries commonly occur. In a **tetragonal distortion of the octahedron**, only the d_{xz} and d_{yz} orbitals remain degenerated. If the ligand is elongated along the z -axis, orbitals with d_z character increase in energy; compression along z has the opposite effect (cf. Fig. 3.3) [24].

Since many natural systems deviate from ideal geometries, the spin-state does not always correspond to a purely HS or LS configuration. Deviations from idealized behavior may arise from several mechanisms. Local distortions of a given crystallographic site can modify bond lengths and angles, thereby altering the ligand field and lifting orbital degeneracies. In addition, pressure- or temperature-induced structural phase transitions may introduce new crystallographic symmetries or coordination environments, leading to fundamentally different ligand-field strengths. Furthermore, iron may redistribute among inequivalent crystallographic sites, each characterized by distinct local symmetries and crystal field parameters [69]. Electron delocalization effects may further complicate the description of spin-states in some systems [70–72].

Another possibility is that iron in different oxidation states inhabits different lattice places, e.g. a migration of Fe³⁺ into another crystallographic site [68]. If Fe²⁺ and Fe³⁺ are both present, it is also possible that the different oxidation states have a spin cross over at different pressures and/or temperatures when coupled to the crystal structure [73] leading to site-specific spin transitions (mixed-spin-state). The so-called intermediate-spin-state, in which only one electron undergoes spin pairing, remains controversial and is therefore not considered further in this work [1, 71, 74–77].

Spin-states, electronic configuration, and electron delocalization can be experimentally

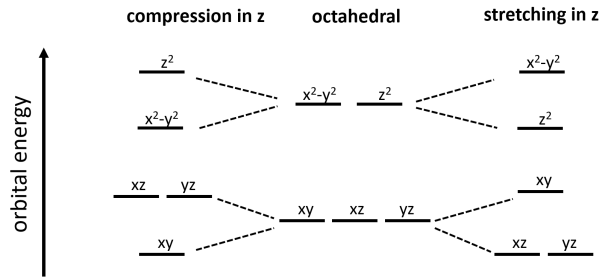


Figure 3.3: Depiction of 3d electron orbitals in distorted symmetries (modified after Janiak et al. [24]).

probed using synchrotron-based spectroscopic techniques, which provide element-specific sensitivity under extreme conditions.

3.2 Non-resonant and resonant X-ray emission spectroscopy

This section outlines the theoretical framework of non-resonant and resonant X-ray emission spectroscopy ((R)XES), which is used in this thesis to probe iron spin-states, oxidation states, and ligand environments. The mathematical treatment is following de Groot and Kotani [26].

(R)XES is a core-level spectroscopic technique based on the interaction between X-rays and matter. In the following, the on-electron approximation will be considered. The effects of electron-electron interactions when using core level spectroscopy will be discussed later in this chapter.

In (R)XES, an incident X-ray photon excites a core electron, thereby creating a core hole (here in the Fe 1s level). The system subsequently relaxes by filling the core hole with an electron from a higher level, emitting an X-ray photon that is detected. Because the excitation and relaxation are coherently linked, (R)XES is described as a second-order scattering process within the Kramers-Heisenberg formalism.

Starting with general process for (R)XES, the incident X-ray photon has an energy of $\hbar\Omega$ with the wavevector $\vec{k}_1$ and a polarization of λ_1 . This photon can excite an electron from the ground state $|g\rangle$ (with energy E_g , where $\Omega = 2\pi c/\lambda$) into an unoccupied orbital. This forces a temporary intermediate state $|i\rangle$ (energy E_i , $\omega = 2\pi c/\lambda$, c as the speed of light and λ as the wavelength), which in turn ends in the final state $|f\rangle$ with the emittance of a photon with an energy of $\hbar\omega$, corresponding wavevector $\vec{k}_2$ and a polarization of λ_2 . The result from the interaction with matter is detectable by observing the emitted photon and provides information about the electronic structure of the excited atom. The final state has the energy E_f which is not equal to E_i [66, 79, 80].

For the photon-electron interaction within the lowest-order perturbation $[e^2/2mc^2] \sum_n A(r_n)^2$ is used and for the second-order perturbation $[e/mc] \sum_n A(r_n)$ is used, with $A(r)$ being the vector potential of the photon. Using the electron mass as m and Planck's constant $\hbar$.

The differential cross section is

$$\frac{d^2\sigma}{d\Omega_{k_2} d(\hbar\omega)} = \frac{\omega^2 V_s}{\hbar c^4} \left(\frac{1}{2\pi} \right)^3 W_{12} \quad (3.1)$$

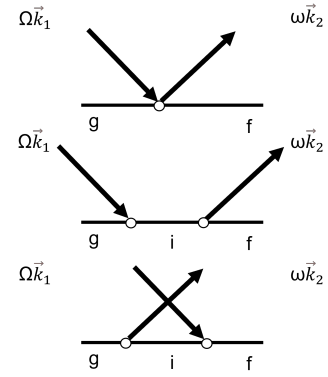


Figure 3.4: Simplified illustration of three different scattering processes. These three processes are the three terms in the square bracket from equation 3.2 (modified after [78]).

at the solid angle Ω_{k_2} with V_s as the volume of the system. W_{12} is the transition rate and is defined as:

$$W_{12} = \frac{2\pi}{\hbar} \sum_j \frac{(2\pi)^2}{\Omega\omega} \left(\frac{e^2 \hbar}{mV_s} \right)^2 \delta(E_g + \hbar\Omega - E_f - \hbar\omega) \times \left| \left[\langle f | \rho_{\vec{k}_1 - \vec{k}_2} | g \rangle (\vec{e}_1 \cdot \vec{e}_2) + \frac{1}{m} \sum_i \left(\frac{\langle f | p(\vec{k}_2) \cdot \vec{e}_2 | i \rangle \langle i | p(-\vec{k}_1) \cdot \vec{e}_1 | g \rangle}{E_i - E_g - \hbar\Omega} + \frac{\langle f | p(\vec{k}_2) \cdot \vec{e}_1 | i \rangle \langle i | p(-\vec{k}_1) \cdot \vec{e}_2 | g \rangle}{E_i - E_g + \hbar\omega} \right) \right] \right|^2 \quad (3.2)$$

where $\vec{e}_1$ (abbreviated from $\vec{e}_{k_1\lambda_1}$) and $\vec{e}_2$ (abbreviated from $\vec{e}_{k_2\lambda_2}$) are the unit vectors of the polarization directions of the incident and emitted photon and:

$$p(\vec{k}) = \sum_n p_n \exp(-i\vec{k}r_n), \quad \rho(\vec{k}) = \sum_n \exp(-i\vec{k}r_n).$$

Equation 3.2 consists of 3 terms describing each a scattering process illustrated in Fig. 3.4. The first one represents the elastic scattering of X-rays by electrons without a change in the internal (electronic) state of the system, whereas the second and third term gain relevance when the incident photon's energy is near or above the energy needed for an excitation of a core electron. This is the case for (R)XES and therefore will be discussed in the following. If the energy of the incident photon is above the excitation threshold, the second order perturbation diverges (due to the fact, that the denominator $E_i - E_g - \hbar\Omega$ is zero), therefore the second term is resonant, and the third term is negligible. Thus, the equation 3.2 can be reduced for (R)XES to as the Kramers-Heisenberg-equation:

$$F(\Omega, \omega) = \sum_f \left| \sum_i \frac{\langle f | T_2 | i \rangle \langle i | T_1 | g \rangle}{E_g + \hbar\Omega - E_i + i\Gamma_i} \right|^2 \delta(E_g + \hbar\Omega - E_f - \hbar\omega). \quad (3.3)$$

Therein T_1 and T_2 describe the radiative transitions induced by the incoming and emitted photons, respectively. To avoid divergences in the case of resonance, the finite lifetime of the intermediate state $|i\rangle$ is taken into account by incorporating the spectral broadening (Γ_i).

If the incident photon energy lies well above the absorption edge, the excited electron is promoted into the continuum and the emission becomes effectively independent of the incident energy (XES). If the incident energy is tuned to the vicinity of the absorption threshold, the scattering amplitude is resonantly enhanced and the emission depends on both incident and emitted energies (RXES).

X-ray emission spectroscopy

Here, the incident photon energy lies well above the absorption edge, promoting an electron into the continuum. This electron is referred to as the photoelectron. Because it is weakly coupled to the remaining valence electrons, the photoelectron does not participate in the subsequent relaxation and emission processes. Under this approximation, the absorption operator T_1 from equation 3.3 can be replaced by the annihilation operator a_c of the core electron, which explicitly represents the creation of a core hole in the initial state. The dipole matrix element associated with the excitation can be approximated by an effective constant transition amplitude, as its energy dependence is negligible far above the edge [26]:

$$F(\Omega, \omega) = \sum_{f'} \int d\epsilon \rho(\epsilon) t^2 \left| \sum_{i'} \frac{\langle f' | T_2 | i' \rangle \langle i' | a_c | g \rangle}{E_g + \hbar\Omega - E_{i'} - \epsilon + i\Gamma_{i'}} \right|^2 \delta(E_g + \hbar\Omega - E_{f'} - \epsilon - \hbar\omega). \quad (3.4)$$

The dipole amplitude t as well as $\rho(\epsilon)$, representing the density of states of the photoelectron, can be assumed to be constant. When the integration over ϵ is carried out, we obtain the following:

$$I(\omega) \sim \rho t^2 \sum_{f'} \left| \sum_{i'} \frac{\langle f' | T_2 | i' \rangle \langle i' | a_c | g \rangle}{E_{f'} - E_{i'} - \hbar\omega + i\Gamma_{i'}} \right|^2. \quad (3.5)$$

It follows that, in the case of XES, the process is independent of the energy of the incident photon [26]. In summary, XES is decoupled from the excitation energy, which lies well above the absorption edge. Since the excitation energy exceeds the binding energy, the interaction between the photoelectron and the remaining electrons is minimal in both the intermediate and final states [79, 81].

Resonant X-ray emission spectroscopy

For RXES, the excitation energy, i.e., the energy of the incident photon, is tuned in the vicinity of the absorption edge of the core electron. Therefore, the Kramers-Heisenberg equation 3.3 can be directly applied to describe the scattering process. Electronic excitations that are dipole forbidden in direct absorption can still be observed, because the two-step excitation-emission process involves intermediate core-hole states that mix orbital symmetries and effectively relax dipole selection rules. Additionally, since RXES depends on both the incident and emitted photon energies independently, it provides additional information about the electronic structure by allowing systematic variation of the excitation energy.

The energy difference between the incident and emitted photons is referred to as the Raman shift, which is element-specific. Because the Raman shift directly corresponds to the excitation process, RXES enables detailed insights into phenomena such as charge transfer, spin-state transitions, and site-specific electronic environments [26].

In practice, RXES data are commonly represented as two-dimensional intensity maps plotted as a function of incident photon energy and either emission energy or energy transfer (energy loss). These maps allow different projections that emphasize complementary aspects of the electronic structure. Constant incident energy (CIE) cuts through the map, yield emission spectra at fixed excitation energy providing L-edge like information. Constant emission energy (CEE) cuts provide high-energy-resolution fluorescence-detected X-ray absorption near-edge structure spectroscopy (HERFD-XANES) spectra. Further information is in Chapter 5.

Relevant electronic transitions

In the previous chapter the concept of (R)XES was described and the concept of transition metals were discussed in 3.1. Here, for this thesis relevant electronic transitions, visible as emission lines in (R)XES, will be presented based on iron as a 3d transition metal. An overview of the transitions, is given in Tab. 3.1. In all these cases, the electron of the $1s$ orbital is excited, creating a hole. Depending on of which orbital's electron fills the hole, a specific emission line is observable.

The $K\alpha$ emission line originates from a radiative decay process following the creation of a $1s$ core hole. When an electron from the $1s$ shell is removed—either by photoionization or resonant excitation—a vacancy is created that can be filled by an electron from the $2p$ shell. The corresponding $2p \rightarrow 1s$ transition results in the emission of a $K\alpha$ photon. Due to spin-orbit splitting of the $2p$ level, the $K\alpha$ line is split into two components: $K\alpha_1$ ($2p_{3/2} \rightarrow 1s$) and $K\alpha_2$ ($2p_{1/2} \rightarrow 1s$) (cf. Fig. 3.6 left) [27, 64]. For RXES the incident photon energy is tuned in the vicinity of the K-absorption edge to create the intermediate $1s$ core hole, where the core-electron is excited into an empty $3d$ orbital, and the subsequent $2p \rightarrow 1s$ decay is measured. Its intensity is approximately eight times stronger than the $K\beta_{1,3}$ emission [64]. The $K\alpha$ line is commonly used for RXES measurements. In this context, the experiment is often referred to as $1s2p$ RXES.

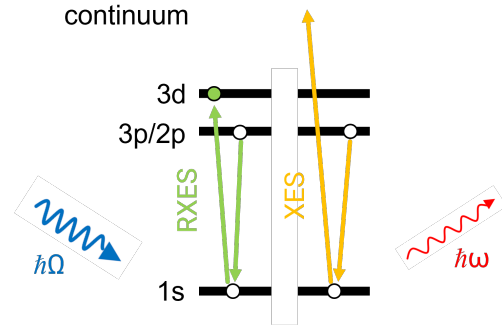


Figure 3.5: Simplified process of RXES (left) and XES (right) sharing the incident $\hbar\Omega$, resulting in a hole in the $1s$ orbital, and emitted photon $\hbar\omega$. This depiction highlights the difference of the excited electron's destination. For RXES the excited electron is promoted to the partially filled $3d$ orbital whereas for XES the electron is excited into the continuum. The hole is either filled by an electron from the $2p$ orbital ($K\alpha$ emission) or $3p$ orbital ($K\beta$ emission).

The $K\beta$ emission is particularly sensitive to the spin-state of iron due to the strong exchange interaction between the $3p$ core hole in the final state and the $3d$ valence electrons. In the HS configuration, the larger number of unpaired $3d$ electrons enhances this exchange interaction, leading to a pronounced $K\beta'$ satellite approximately 15 eV below the main $K\beta_{1,3}$ peak [27, 64]. As the system undergoes a transition to the LS state, the number of unpaired $3d$ electrons decreases, reducing the exchange splitting and causing the $K\beta'$ feature to strongly diminish (cf. Fig. 3.6 middle). This makes the $K\beta$ emission a powerful qualitative probe of the iron spin-state. For XES, the incident photon energy is tuned well above the absorption edge to create a $1s$ core hole via photoionization into the continuum. The emitted $K\beta$ radiation is then recorded as a function of emission energy, which is commonly denoted as $1s3p$ XES.

Table 3.1: Overview of the emission lines and their origin as well as measurement technique and alternative name.

hole	excited to	filling electron	emission line	method	notation
$1s$	empty $3d$	$2p$ ($2p_{3/2}$, $2p_{1/2}$)	$K\alpha$ ($K\alpha_1$, $K\alpha_2$)	RXES	$1s2p$ RXES
$1s$	empty $3d$	$3p$	$K\beta_{1,3}$, $K\beta'$	RXES	$1s3p$ RXES
$1s$	continuum	$2p$ ($2p_{3/2}$, $2p_{1/2}$)	$K\alpha$ ($K\alpha_1$, $K\alpha_2$)	XES	$1s2p$ XES
$1s$	continuum	$3p$	$K\beta_{1,3}$, $K\beta'$	XES	$1s3p$ XES
$1s$	continuum	$3d/2p$ from ligand	$K\beta_{2,5}$	XES	vtc
$1s$	continuum	$3d/2s$ from ligand	$K\beta''$	XES	vtc

The third, here relevant, emission line stems from valence-to-core (vtc) de-excitation processes involving occupied valence states with mixed metal–ligand character. In contrast to the $K\alpha$ and $K\beta_{1,3}$ lines, which originate from core-level transitions, vtc emission arises from valence orbitals that possess significant p -like character and can therefore decay

into the $1s$ core hole via dipole-allowed transitions. The $K\beta_{2,5}$ feature primarily reflects ligand $2p$ states hybridized with Fe $3d$ orbitals, although minor contributions from Fe $4p$ states may also be present due to metal-ligand orbital mixing [26, 82]. Consequently, this emission line is highly sensitive to the chemical environment and degree of covalency of the Fe-ligand bond. The $K\beta''$ feature mainly arises from deeper-lying ligand $2s$ states with admixture of metal orbitals. Its energy position depends strongly on the ligand identity, while its intensity and spectral shape are influenced by bond length and metal-ligand overlap (cf. Fig. 3.6 right) [26, 82].

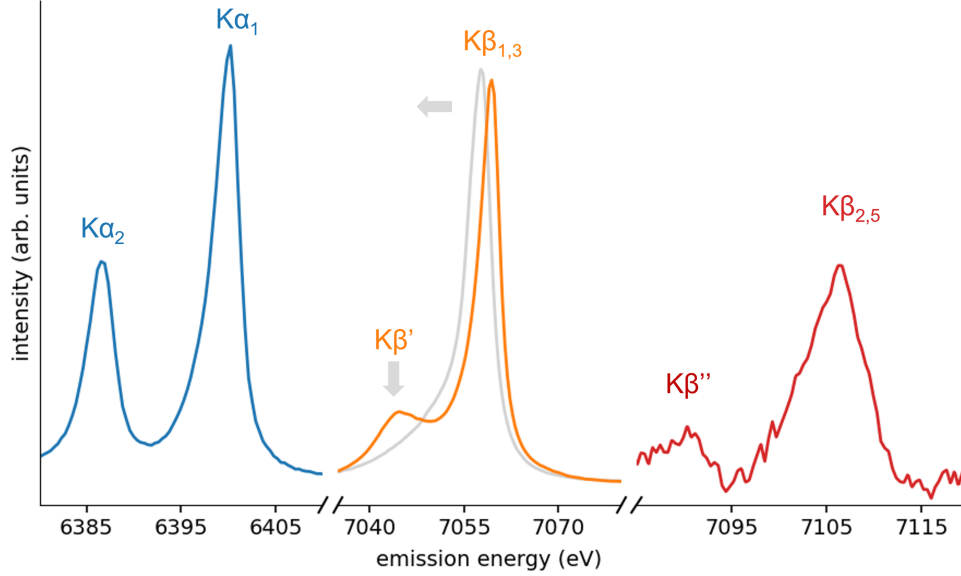


Figure 3.6: Different emission lines, with scaled intensity for comparison. **Left)** $K\alpha$ emission line split into $K\alpha_1$ and $K\alpha_2$. **Middle)** Main $K\beta_{1,3}$ line and $K\beta'$ shoulder. In orange the HS state and in light grey as LS state showing the main peak shift to lower energies and decrease of the shoulder intensity while shifting to main line. **Right)** Vtc emission with the $K\beta_{2,5}$ peak and the $K\beta''$ pre-peak.

3.3 X-ray absorption near-edge structure spectroscopy

XANES complements XES by extending the sensitivity from the occupied electronic states to the unoccupied or partially occupied states and to the local geometric environment surrounding the absorbing atom. In this thesis, the conceptual and mathematical treatment of XANES follows de Groot and Kotani [26] and Henderson et al. [83].

Within the general formalism of X-ray absorption spectroscopy, the absorption coefficient is described by Fermi's golden rule, which gives the transition rate from a ground state $|g\rangle$ to a set of final states $|f\rangle$ as

$$W_{g \rightarrow f} = \frac{2\pi}{\hbar} |\langle f|T|g\rangle|^2 \delta(E_f - E_g - \hbar\Omega), \quad (3.6)$$

where T is the transition operator, related to interaction Hamiltonian H_{int} between the electromagnetic field and the electrons, $\hbar\Omega$ is the incident photon energy, and E_g and E_f

are the energies of the ground and final states, respectively. H_{int} reduces to the dipole operator, and the X-ray absorption coefficient $\mu(\Omega)$ becomes

$$\mu(\Omega) \propto \sum_f |\langle f | \vec{\epsilon} \cdot \vec{r} | g \rangle|^2 \delta(E_f - E_g - \hbar\Omega), \quad (3.7)$$

with $\vec{\epsilon}$ the photon polarization vector and $\vec{r}$ the position operator. Further, the term $|\langle f | \vec{\epsilon} \cdot \vec{r} | g \rangle|^2$ can be approximated by the squared matrix element M^2 and the delta function $\delta(E_f - E_g - \hbar\Omega)$ representing the density of empty states ρ . This results in:

$$I_{XANES} \approx M^2 \rho. \quad (3.8)$$

In the near-edge region, the relatively low kinetic energy of the excited photoelectron enhances multiple-scattering pathways and increases the sensitivity to the local unoccupied density of states. In this regime XANES is sensitive to oxidation state, coordination geometry, and symmetry [26, 83].

At the Fe K-edge, a $1s$ electron is excited into unoccupied states (bound and continuum-like), and several characteristic energies are commonly distinguished (cf. Fig. 3.7):

- **Pre-edge region**, corresponding to the lowest-energy bound-state resonance. In this region, the $1s$ electron is excited into localized unoccupied states with predominantly $3d$ character. The transition is formally quadrupole allowed, but gains significant dipole intensity through $3d$ - $4p$ mixing induced by symmetry lowering as well as through hybridization between Fe $3d$ and ligand $2p$ orbitals. Consequently, the pre-edge features are highly sensitive to iron oxidation state, covalency, and local coordination geometry [84, 85].
- **Rising of the main edge (absorption onset)**, where the absorption coefficient increases steeply as the photon energy approaches the ionization threshold and transitions into the lowest electron-hole excited state [83]. The energy position of this onset shifts systematically with oxidation state due to changes in the effective nuclear charge and core-level binding energy.
- **Main edge peak (edge resonance)**, representing a strong enhancement of absorption just above the edge [83]. The position of the absorption edge relies on oxidation state and inter-atomic distances [86, 87].
- **Post-edge (multiple scattering region)**, where the excited photoelectron undergoes multiple scattering from neighboring atoms [88], producing broader spectral features that reflect medium-range structural order [89].

Beyond the XANES region is the extended X-ray absorption fine structure (EXAFS) regime, characterized by oscillatory modulations in the absorption coefficient arising from single- and multiple-scattering of the photoelectron by neighboring atoms [90]. This regime is mentioned here solely for completeness and general classification.

In practice, the edge energy is defined operationally, for example by the maximum of the first derivative of the spectrum or by a fixed fraction of the total edge step, and it is essential to apply one consistent definition when comparing different samples, particularly in Fe-bearing materials where the edge may show multiple inflection points or leading-edge shoulders [26, 83].

The pre-edge region, typically located about 10-20 eV below the main edge, contains relatively weak but important characteristic features associated with transitions into

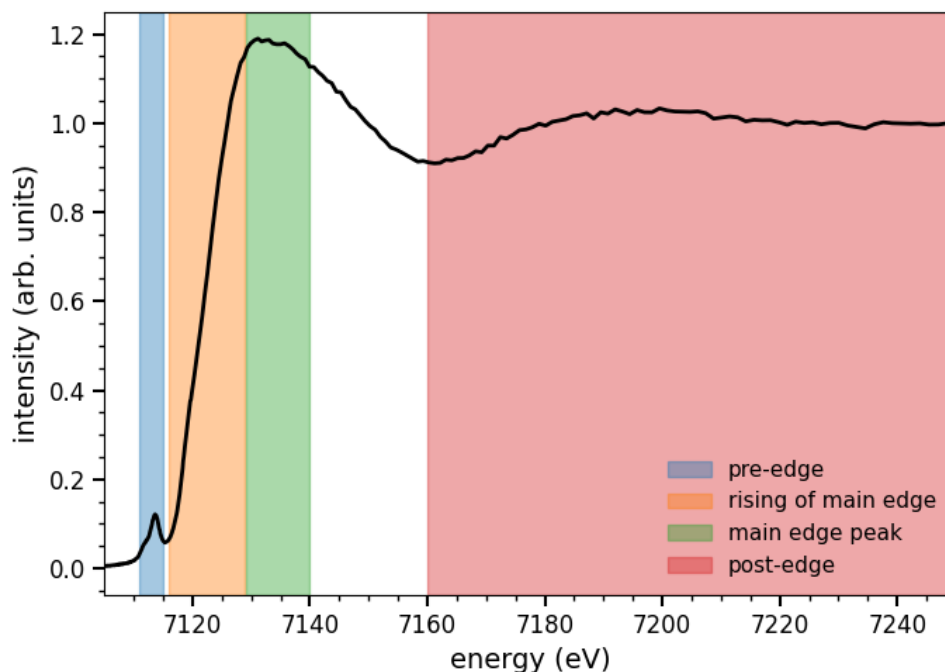


Figure 3.7: XANES spectrum with the colored regions marking the pre-edge (blue), rising of the main edge (orange), main edge peak (green) and post edge region (red).

predominantly 3d-derived states. Two main types of transitions contribute: (i) Electric quadrupole transitions from the 1s level into 3d states also contribute to the pre-edge intensity. While the $1s \rightarrow 3d$ transition is dipole-forbidden ($\Delta l = \pm 1$), it is allowed as an electric quadrupole ($E2$) transition with $\Delta l = \pm 2$. Quadrupole transitions are intrinsically weaker than dipole transitions but can become observable in centrosymmetric environments due to the substantial density of unoccupied 3d states; and (ii) electric dipole transitions into mixed 3d-4p states. When inversion symmetry is broken, for example in tetrahedral coordination, 3d and 4p orbitals hybridize. Only the subset of Fe 3d orbitals that transforms like the 4p representation mixes strongly and acquires dipole-allowed character, leading to intense pre-edge peaks, whereas the remaining 3d states retain mainly quadrupole character [26, 83, 91].

The relative contributions of dipole and quadrupole transitions are governed by site symmetry, metal-ligand bond lengths, and the degree of 3d-4p mixing. Polarized XANES and HERFD measurements show that both channels can be significant in transition-metal oxides, including non-local transitions mediated by ligands [85, 87]. Systematic studies across the 3d series demonstrate that pre-edge intensity is highly sensitive to coordination symmetry: fourfold-coordinated sites, such as tetrahedral Fe^{3+} , exhibit much stronger pre-edge features than octahedral sites because of the absence of an inversion center and the associated increase in hybridization [83]. For a given oxidation state, the pre-edge intensity generally decreases with increasing coordination number (tetrahedral > trigonal bipyramidal > octahedral) [26, 83].

Variations in metal-oxygen bond length further modulate pre-edge intensity. Shorter metal-ligand distances enhance covalency and orbital overlap, increasing the degree of 3d-4p mixing and thereby strengthening the pre-edge feature [92]. As a result, tetrahedrally

coordinated Fe^{3+} , which combines short Fe-O distances with the absence of inversion symmetry, exhibits substantially higher pre-edge intensities than octahedral Fe^{3+} [84]. Across the $3d$ transition metals, early elements display stronger pre-edge features than later ones, and Fe^{3+} shows a moderate pre-edge intensity that remains strongly dependent on coordination geometry [92].

Wilke et al. investigated Fe^{2+} in four-, five-, six-, eight-, and twelve-fold coordination and Fe^{3+} in four-, five-, and six-fold coordination. They demonstrate that octahedrally coordinated Fe^{2+} and Fe^{3+} typically exhibit two to three pre-edge components, which arise from crystal-field splitting of the $3d$ manifold into lower-energy (t_{2g}) and higher-energy (e_g) subsets. In addition, the relative intensities and energy separation of these components are influenced by the spin-state of iron, as HS and LS configurations differ in $3d$ occupancy and exchange interactions, which modify the multiplet structure of the final states. Tetrahedral Fe^{3+} is often dominated by a single intense pre-edge peak. The energy centroid of the pre-edge band shifts systematically from lower values for Fe^{2+} to higher values for Fe^{3+} , providing a robust indicator of the average iron oxidation state. The integrated pre-edge area correlates strongly with site symmetry and distortion: the weakest pre-edges occur in centrosymmetric, nearly regular octahedral sites, while the strongest appear in tetrahedral Fe^{3+} or strongly distorted octahedral environments. When combined with independent constraints on coordination, the combination of pre-edge centroid and integrated area, XANES enables quantitative estimates of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ in crystalline and amorphous silicates [84].

The position of the main absorption edge also tracks changes in formal oxidation state. For many $3d$ transition metals, the edge energy often increases approximately linearly with effective valence, with typical shifts on the order of a few eV per unit change in oxidation state. Pre-edge energies generally shift at a smaller rate, so the energy separation between the main edge and the pre-edge peak provides an additional proxy for oxidation state. These trends have been established for several oxide systems, including iron oxides, and are widely exploited in mixed-valence materials where multiple iron coordination environments coexist. At the same time, interpretation of pre-edge and edge positions can be complicated by overlapping contributions from different sites, structural disorder, and covalency effects, so reliable quantitative analysis usually requires comparison to appropriate reference compounds and, where possible, theoretical simulations [26, 83].

3.4 X-ray diffraction

XRD is a fundamental technique to determine the structure of crystalline materials. It is primarily sensitive to long-range crystallographic order and therefore provides strong constraints on phase assemblages, unit-cell parameters, and symmetry. In high-pressure studies, systematic peak shifts track compression of the lattice, whereas the appearance, disappearance, or splitting and intensity of reflections provide clear fingerprints of structural phase transitions. Peak widths and intensity distributions in 2D diffraction pattern can further contain information on crystallite size and preferred orientation [65, 93].

XRD enables phase identification and the quantification of crystallographic parameters by analyzing the characteristic interference patterns of scattered X-rays. The theoretical background presented here follows the works of Cullity et al. [65] and Warren et al. [93].

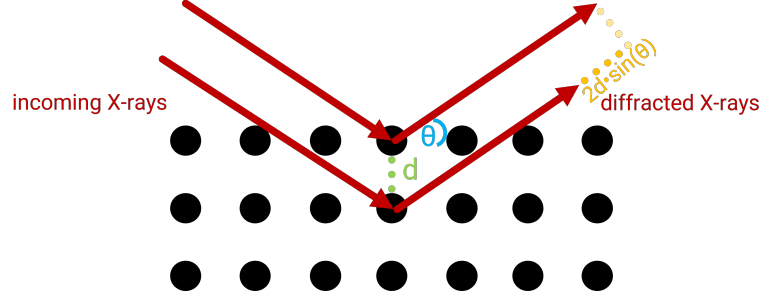


Figure 3.8: Simplified process of the Bragg's law, where the incident X-rays are diffracted at the lattice. The angle for the diffraction process is Θ and d as the lattice distance, resulting in a difference of path of $2d \sin \Theta$.

When X-rays are incident on a crystalline material, they interact predominantly with the bound electrons of the atoms and are elastically scattered. The oscillating electromagnetic field of the incident X-ray beam induces oscillatory motion of these electrons, which then re-emit radiation without a change in energy. Because the atoms are arranged periodically in a crystal lattice, the scattered waves can interfere constructively at specific angles when their path-length difference equals an integer multiple of the X-ray wavelength. This condition is commonly expressed by Bragg's law [65]:

$$\lambda = 2d \sin \Theta, \quad (3.9)$$

where λ is the X-ray wavelength, d is the spacing between crystallographic lattice planes, and Θ is the angle between the incident beam and the reflecting lattice planes, the so-called Bragg-angle. Bragg's law provides a simple geometrical description of diffraction as reflection from lattice planes and directly links the positions of diffraction peaks to interplanar spacings and crystal symmetry (Fig. 3.8) [65].

For XRD incident and scattered beams lie in the same plane and are described by their respective wave vectors $\vec{k}$ and $\vec{k}'$. The angle between the directions of the incident and diffracted beams is defined as 2Θ . The wave vector transfer or scattering vector, defined as

$$\vec{q} = \vec{k}' - \vec{k}, \quad (3.10)$$

has a magnitude

$$|\vec{q}| = \frac{4\pi}{\lambda} \sin \Theta, \quad (3.11)$$

which depends on the scattering angle Θ and the X-ray wavelength λ [65, 93].

The total scattering amplitude $A(\vec{q})$ results from the coherent (phase-preserving) sum of elastic scattering contributions from all atoms:

$$A(\vec{q}) = \sum_n f_n(\vec{q}) e^{i\vec{q} \cdot \vec{r}_n}, \quad (3.12)$$

where $\vec{r}_n$ is the position of atom n in the crystal, and $f_n(\vec{q})$ is the atomic form factor, which accounts for the spatial distribution of the atomic electron density. The form factor decreases with increasing scattering angle (or momentum transfer) because of destructive interference between waves scattered by different parts of the extended electron density within the atom [65, 93].

The measurable intensity is linked to the square of the scattering amplitude's magnitude:

$$I(\vec{q}) \propto |A(\vec{q})|^2 \quad (3.13)$$

This relationship reflects the wave nature of X-rays, where observable intensity arises from the interference of amplitudes. Crystalline periodicity allows further simplification. Atomic positions can be expressed as a combination of a lattice translation vector $\vec{r}_j = a\vec{x} + b\vec{y} + c\vec{z}$, where $a, b, c \in \mathbb{Z}$ and $\vec{x}, \vec{y}, \vec{z}$ are the lattice basis vectors, and a basis vector $\vec{\delta}_k$ describing the position of atom k within the unit cell: $\vec{r}_{jk} = \vec{r}_j + \vec{\delta}_k$. Substituting into the scattering amplitude expression yields to a factorized form:

$$A(\vec{q}) \propto F(\vec{q}) \cdot S(\vec{q}) \quad (3.14)$$

with the structure factor as:

$$S(\vec{q}) = \sum_k f_k(\vec{q}) e^{i\vec{q} \cdot \vec{\delta}_k} \quad (3.15)$$

and the lattice sum:

$$F(\vec{q}) = \sum_j e^{i\vec{q} \cdot \vec{r}_j}, \quad (3.16)$$

with j as the sum over all unit cells. Constructive interference, and thus detectable diffraction intensity, can only occur when the Laue condition is fulfilled:

$$\vec{q} = \vec{G}_{hkl} \quad (3.17)$$

Here, $\vec{G}_{hkl}$ is a reciprocal lattice vector corresponding to the Miller indices (h, k, l) . This condition defines the allowed scattering directions and is mathematically equivalent to Bragg's law. It directly links the observed diffraction peaks positions to the underlying crystal structure (i.e. lattice spacing and symmetry) [65, 93]. The corresponding diffraction intensity is governed by the structure factor $S(\vec{q})$, which encodes the atomic scattering factors and their spatial arrangement within the unit cell. Notably, fulfillment of the Laue condition $\vec{q} = \vec{G}_{hkl}$ does not guarantee a non-zero reflection; destructive interference may result in $S(\vec{G}_{hkl}) = 0$, giving rise to systematic absences characteristic of the crystal symmetry.

Diffraction recorded on a two-dimensional area detector provides direct information on crystallite orientation and texture. For polycrystalline (powder) samples, many crystallite orientations satisfy the diffraction condition simultaneously, producing Debye-Scherrer rings. The ring appearance provides immediate qualitative information: continuous, smooth rings indicate good powder averaging, whereas spotty rings or discrete reflections (speckles) suggest a limited number of large crystallites, grain growth, or preferred orientation [65, 93].

Quantitative analysis is also performed on a one-dimensional pattern obtained by azimuthal integration of the 2D detector image. The resulting intensity profile $I(2\Theta)$,

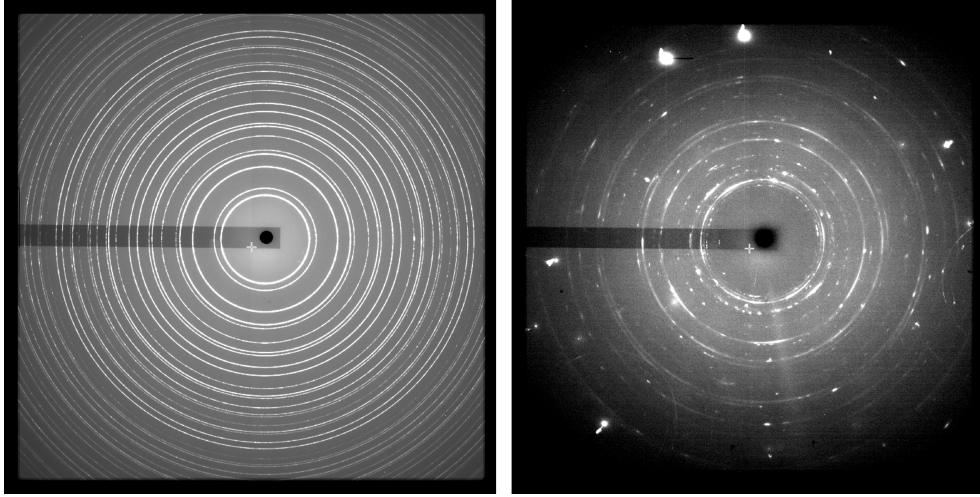


Figure 3.9: Depiction of XRD detector images. **Left)** Calibration material CeO_2 showing clear Debye-Scherrer rings. **Right)** Fe_2O_3 after heating at 80 GPa with speckles along rings from rhenium and diamond.

$I(q)$ or $I(d)$ contains peak positions, widths, and relative intensities that can be tracked as a function of pressure or temperature [65, 93]. The evolution of the peak positions or new reflections reflect structural changes [65, 93]:

- **New peaks appear:** creation of a new phase or the onset of a phase transition.
- **Peaks disappear:** consumption of the original phase, transformation completion, or loss of crystallinity.
- **Peak splitting:** symmetry lowering or removal of reflection degeneracies.
- **Systematic peak shift without new peaks:** elastic compression/expansion within the same phase (lattice parameter change).
- **Coexistence of two peak sets:** two-phase region, metastability, or pressure gradients in high-pressure experiments.

3.5 Synchrotron Mössbauer spectroscopy

SMS is used in this thesis as a complementary probe to XES and XANES. In contrast to those techniques, which are primarily sensitive to the electronic structure of all absorbing atoms along the beam path, SMS directly measures the nuclear resonant response of ^{57}Fe isotope. This provides quantitative constraints on the oxidation state (Fe^{2+} versus Fe^{3+}), spin-state, and local coordination environment of iron through the analysis of hyperfine interactions [1, 2, 94, 95].

The underlying physical phenomenon is the Mössbauer effect: the recoilless resonant emission and absorption of γ -rays by atomic nuclei [95, 96]. For an isolated ^{57}Fe nucleus, emission of the 14.4 keV γ -ray would normally impart a recoil energy of ~ 2 meV, which is many orders of magnitude larger than the natural linewidth of the nuclear transition (~ 4.6 neV). In this case, the emitted and absorbed photon energies would not match exactly, and nuclear resonance would be effectively suppressed [2, 95]. When the emitting (or absorbing) nucleus is rigidly bound in a solid matrix, however, the recoil momentum

can be taken up by the entire structure. The recoil energy per atom then becomes negligibly small and a significant fraction of events occur without energy loss to phonons. These recoilless events enable resonant nuclear absorption with extremely high energy resolution, which is the basis of Mössbauer spectroscopy [2].

In a conventional laboratory Mössbauer experiment, the energy of the ^{57}Fe isotope resonance is scanned by mechanically moving either γ -source or absorber and exploiting the relativistic Doppler effect. In SMS, by contrast, the resonant radiation is derived from a highly monochromatic synchrotron beam.

Energy-domain SMS and time-domain nuclear forward scattering (NFS) represent two complementary synchrotron-based approaches to Mössbauer spectroscopy. In SMS, monochromatic γ -radiation resonant with the ^{57}Fe nuclear transition is generated using a nuclear resonant monochromator crystal (commonly $^{57}\text{FeBO}_3$). The energy of the incident radiation is scanned via the Doppler effect, typically by controlled motion of the nuclear resonant crystal, producing an energy spectrum analogous to conventional Mössbauer spectroscopy. In this case, the measured spectrum reflects the energy-dependent resonant absorption cross section of ^{57}Fe nuclei in the sample and can be interpreted as a linear superposition of contributions from different iron sites or electronic states [94, 97]. In contrast, NFS represents the time-domain analogue of Mössbauer spectroscopy. Short synchrotron pulses excite the resonant nuclei, and the delayed forward-scattered intensity is recorded as a function of time. The resulting time spectrum exhibits characteristic quantum-beat patterns that arise from interference between different hyperfine-split nuclear transitions and therefore contain information about the hyperfine interactions in the sample [94].

The ^{57}Fe nucleus is particularly well suited for Mössbauer spectroscopy. Its ground state has nuclear spin $I = 1/2$, and the first excited state at 14.4125 keV has $I = 3/2$, giving rise to a simple and well-understood multiplet structure. The relatively long lifetime of the excited state (~ 141 ns) leads to a very small natural linewidth ($\Delta E \approx 4.6 \times 10^{-9}$ eV) and thus exceptionally sharp resonances [95]. Hyperfine interactions between the nuclear states and their surrounding electronic and magnetic environment lift degeneracies of the nuclear levels and split the resonance into discrete components (Fig. 3.10). The three standard hyperfine parameters are [2, 95, 98]:

- **Isomer shift** (δ): A measure of the s-electron density at the nucleus, referenced to a standard absorber. It is sensitive to the oxidation state (Fe^{2+} , Fe^{3+}), indirectly to spin-state and, to a lesser degree, coordination and bonding environment.
- **Quadrupole splitting** (ΔE_Q): Splitting of the nuclear levels due to the interaction of the nuclear quadrupole moment with the electric field gradient (EFG) at the nucleus. The EFG arises from both the asymmetric distribution of surrounding ligands and the anisotropic distribution of valence electrons. Consequently, quadrupole splitting reflects deviations from cubic symmetry and provides information about site distortion and coordination geometry. In addition, the electronic contribution to the EFG makes ΔE_Q indirectly sensitive to the spin-state of iron:

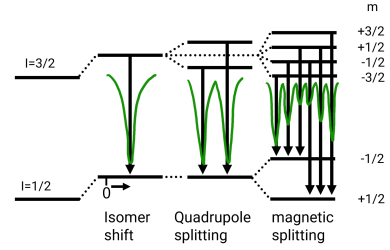


Figure 3.10: Simplified illustration of hyperfine splitting of nuclear energy levels and the corresponding Mössbauer spectra in green (modified after [2]).

HS configurations often produce a more symmetric $3d$ charge distribution and thus smaller EFGs, whereas LS states can yield larger quadrupole splittings even at identical coordination environments.

- **Magnetic hyperfine splitting (ΔE_M):** Splitting in the presence of an internal or applied magnetic field at the nucleus. For iron-bearing oxides and silicates this is mainly relevant in magnetically ordered phases; in paramagnetic glasses only quadrupole doublets are expected at room temperature.

For a single, well-defined crystallographic site, each resonance line has, in principle, a Lorentzian line shape determined by the lifetime of the excited nuclear state [2, 95]. In normal materials, especially in glasses and disordered minerals, there is a distribution of local environments (e.g. bond lengths, site distortions). These structural variations, together with instrumental broadening and finite absorber thickness, broaden and sometimes distort the lines away from a simple Lorentzian profile. Thus, these effects can be approximated by convoluting the intrinsic Lorentzian with a Gaussian distribution of hyperfine parameters, leading to a Voigt or pseudo-Voigt line shape [94, 99, 100]. Hence, the natural linewidth is Lorentzian, whereas the Gaussian component captures ‘smearing’ due to distributions of quadrupole splittings and isomer shifts in structurally disordered sites.

In an ideal paramagnetic quadrupole doublet representing a single Fe site in a glass, the two lines are expected to be symmetric, with equal areas and identical widths, and separated by the quadrupole splitting ΔE_Q . Significant asymmetry within a doublet (e.g. one line broader or more intense than the other) typically indicates thickness effects, overlapping components, or an unresolved distribution of hyperfine parameters [16, 99]. Voigt-based or Gaussian-broadened Lorentzian fits allow such asymmetry of the envelope to be modeled by a single doublet with distributed hyperfine parameters, rather than by artificially adding multiple discrete doublets [94, 95, 99].

In Fe-bearing silicate glasses, the hyperfine parameters can be used as semi-quantitative fingerprints for Fe valence, spin-state, and coordination [16, 22]. At ambient pressure and temperature:

- High-spin Fe^{2+} typically exhibits relatively large isomer shifts (δ) and moderate to high quadrupole splittings (ΔE_Q), reflecting larger ionic radii and more distorted 6-fold (VI, octahedral), 5-fold (V, trigonal bipyramidal) or 4-fold (IV, tetrahedral) coordinated sites [22, 95].
- High-spin Fe^{3+} shows smaller isomer shifts and moderate quadrupole splittings. Fe^{3+} commonly occupies tetrahedral or octahedral sites, depending on composition and oxygen fugacity [13, 22].

Qualitative ranges for the parameters discussed above are summarized in Table 3.2.

With increasing pressure, both Fe^{2+} and Fe^{3+} in depolymerized basaltic melts and glasses are expected to shift toward higher coordination numbers and, in some cases, undergo spin transitions [1, 14, 22]. Fe^{3+} tends to transform from predominantly tetrahedral coordination at low pressure to octahedral coordination at higher pressure. These structural changes are commonly accompanied by a decrease in isomer shift and modifications of the quadrupole splitting [3, 22]. However, a reduction in isomer shift can also arise from pressure-induced spin transitions, and therefore the observed spectral

changes may reflect contributions from both coordination and electronic effects. High-spin Fe^{2+} in basaltic compositions is dominantly 5- to 6-fold coordinated, even at low pressure; 4-fold Fe^{2+} is rare and is stabilized mainly in very depolymerized, low-pressure melts [14, 22]. Upon compression, Fe^{2+} is driven towards more compact octahedral environments, typically accompanied by decreasing δ and a narrowing of the quadrupole splitting distribution, although similar trends may also occur if pressure induces a HS to LS transition [16, 22].

For the interpretation of the SMS data in this thesis, it is therefore useful to define approximate isomer-shift-quadrupole-splitting ranges in $(\delta, \Delta E_Q)$ space that correspond to Fe^{2+} and Fe^{3+} in different coordination and spin-states. These ranges are compiled from Dyar et al. [99] and are summarized in Table 3.2. They provide a framework for assigning the Fe^{2+} and Fe^{3+} components in the high-pressure haplobasaltic glasses measured here, and for tracking systematic changes in coordination (cf. 6.4.2).

Table 3.2: Approximate isomer-shift and quadrupole-splitting ranges for Fe^{2+} and Fe^{3+} in oxide glasses at ambient temperature, extracted from [99]. Values are indicative and may shift slightly with composition, pressure and temperature.

species	context	δ (mm/s)	ΔE_Q (mm/s)
Fe^{2+} (IV, tetrahedral)	rare in basaltic glasses	0.90-1.05	0.86-1.63
Fe^{2+} (VI, octahedral)	common in basaltic glass	0.98-1.28	1.11-3.30
Fe^{2+} (VIII, cubic)	not observed in basaltic glasses	1.18-1.33	2.88-3.79
Fe^{3+} (IV, tetrahedral)	LP*, depolymerized setting	0.18-0.27	0.16-0.85
Fe^{3+} (VI, octahedral)	HP†, polymerized setting	0.23-0.50	0.46-1.32
$\text{Fe}^{2.5+} \ddagger$	mixed-valence environments	0.61-0.80	0.51-1.61

* low-pressure

† high-pressure

‡ Delocalization of electrons between Fe^{2+} and Fe^{3+} , averaged isomer-shift value.

Because Mössbauer spectroscopy directly distinguishes between Fe^{2+} and Fe^{3+} through their characteristic isomer shifts and quadrupole splittings, SMS enables determination of the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio *in situ* at high pressure. Combined with thermodynamic models such as those of Kress and Carmichael [101] and their high-pressure extensions for silicate melts, Mössbauer-derived $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios can be translated into oxygen fugacity $f\text{O}_2$ (further information on oxygen fugacity in Section 2.3).

In mantle petrology, redox conditions are routinely expressed relative to mineral redox buffers. Common reference assemblages include the iron-wüstite buffer (IW), the nickel-nickel oxide buffer (NNO), the fayalite-magnetite-quartz buffer (FMQ), and the magnetite-hematite buffer (MH). These buffers define thermodynamically constrained $f\text{O}_2$ - T relations, and redox states are typically reported as ΔIW , ΔFMQ , or ΔNNO . Anchoring Mössbauer-derived $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios to such buffers allow for direct comparison of high-pressure redox states across different compositions and experiments [101].

In the context of this thesis, SMS therefore not only provides information about Fe coordination and electronic configuration, but also offers a quantitative window into the redox conditions governing Fe-bearing oxides and haplobasaltic melts. This complements the deep-mantle redox framework introduced in Chapter 2 and allow direct evaluation of how pressure-induced structural and electronic transitions in iron influence the oxygen budget and melt dynamics of the lower mantle.

4 Experimental setup

Recreating the extreme conditions of Earth’s lower mantle in the laboratory is essential for understanding the behavior of materials at depth, yet reproducing these conditions presents substantial experimental challenges. The lower mantle extends from approximately 660 km to 2900 km below the Earth’s surface [9, 32], corresponding to pressures between 24 GPa and 136 GPa [9, 10]. Temperatures within this region vary considerably: near the top, estimates are around 2000 K, while values at the CMB range from approximately 2600 K to 3500 K [10, 36], depending on the applied geophysical model.

This chapter describes the methods for achieving such HP/HT conditions in a laboratory setting. Particular emphasis is placed on techniques compatible with *in situ* X-ray spectroscopy, which enables real-time probing of structural and electronic changes under extreme conditions.

4.1 Diamond anvil cells

In the experiments in this thesis, pressures of up to 120 GPa were achieved using diamond anvil cells (DACs), where the high pressures are created by pressing the flattened tips of the diamonds against each other. This section provides details on the DACs, diamond types, methods of pressure determination, and the applied scattering and emission geometries.

Generally, present-day DACs are able to reach pressures into the several-hundred-GPa range [102–107] and even up to the TPa regime [108]. Double-staged DACs make this possible with a first stage of conventional diamonds combined with secondary anvils carrying miniature culets [109].

An overview of all DAC configurations and diamond types, including sample photographs, is provided in the Appendix A.2.

4.1.1 BX90-RD DAC

The DAC type used in this thesis is a custom-built design developed by Kantor et al. [110] referred to as BX90-RD. Its defining feature is a radial opening on two sides allowing a $\sim 70^\circ$ scattering angle for a more efficient data acquisition. The principle of the cell is illustrated in Fig. 4.1 (redrawn after Kantor et al. [110]). The DAC consists of two main components, the outer cylinder (dark gray, B) and the inner piston (light gray, A). In both, piston and outer cylinder, is a tungsten carbide seat (grey, D) positioned on which a diamond (light turquoise, E) is glued. Between the diamond a rhenium gasket (light blue, C) is placed, containing a drilled hole that serves as the sample chamber and holds additionally the pressure transmitting medium. A detailed description of diamond alignment, gluing, and DAC loading procedures is provided in

Appendix A.1. The diamond seat can be adjusted and fixated in its position by using 4 setscrews (brown, F). The pressure can be increased by using 4 screws (M4 (#8-32), orange, G) in combination with washers (Belleville springs, blue, H) which must be tightened diagonally. During gas loading, the safety screws (pink, I) ensure that the diamonds remain mechanically decoupled to prevent unintended contact.

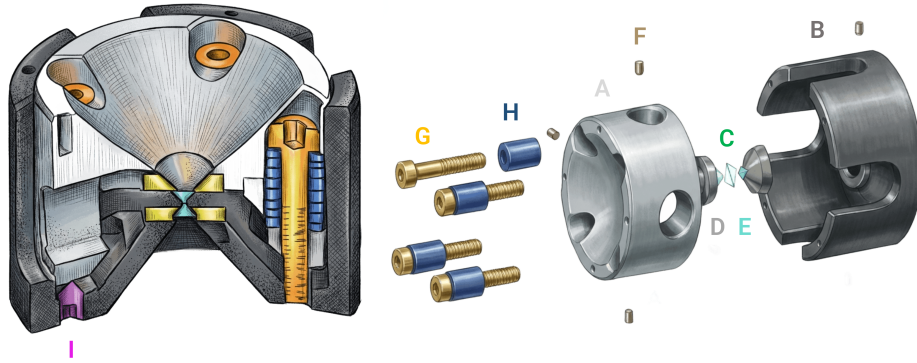


Figure 4.1: Sketch of a DAC Type BX90-RD with a inner side-view (left) and exploded view (right). The DAC consists of (A) inner piston, (B) outer cylinder, (C) rhenium gasket, (D) tungsten carbide seats, (E) diamonds, (F) setscrews, (G) screws, (H) washers and (I) safety screw (redrawn after Kantor et al. [110] and improved with AI [35]).

Advantages of the BX-90RD, beside the radial opening is, the option to use asymmetrical seats. Meaning, the height of the standard diamond seat is increased whereas the height of the Boehler-Almax or miniature diamond seat is decreased. In combination with a gasket flip (described in App. A.1.2) providing different indentation depths, the emission angle can be further optimized for a better scattering geometry (cf. Chap. 4.3) [111].

4.1.2 Diamonds

In a DAC, high pressure is generated by pressing the flattened tips of the diamonds, so called culets, against each other. The culet size is decisive for the pressure that can be achieved. Thus, smaller culets allow higher pressures to be achieved, following $p = \frac{F}{A}$. The pressure p is determined by the force F applied on an area A . In this thesis culet sizes between 200 and 120 μm were used. To further increase the diamonds' mechanical stability, beveled diamonds can be employed (300 μm bevel in this thesis) [109], the depiction of a beveled diamond is to be seen in Fig. 4.2a.

Three different types of diamond designs, manufactured by Almax easyLab, were used in this study (Fig. 4.2b) [112]. The standard diamond (ST, design P01006, Type Ia) is either coupled with the Boehler-Almax diamond (BA, design P01036, Type Ia) or the miniature diamond (MD, design P01942, Type Ia), where the latter is a miniature version of the BA diamond as the name implies. The ST diamond has a height of 2.72 mm, and its cut differs vastly from the BA and MD designs. This difference in shape is highly suitable for (R)XES measurements, exploiting the steep angle for detecting emission through the radial opening of the BX90-RD (a more detailed explanation is given in Chapter 4.3). A combination of the ST diamond with the BA diamond is feasible and

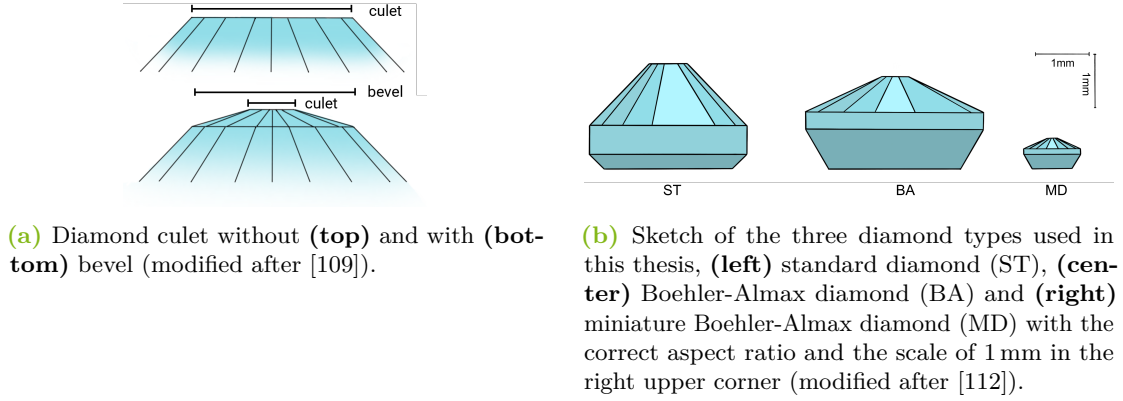


Figure 4.2: Sketch of culet configurations (**left**) and diamond types (**right**).

well suited for conventional XES measurements. However, owing to its comparatively large height of 1.72 mm, the BA diamond is not optimal for RXES experiments. For RXES, the MD diamond, with a reduced height of 0.5 mm, is therefore preferred on the upstream side. The shorter diamond path length minimizes absorption of the incident X-ray beam, resulting in a higher photon flux at the sample and, consequently, an enhanced detectable emission signal. In numbers, replacing the BA diamond with an MD diamond during XES, increases the photon flux on the sample at 10 keV by roughly a factor of ≈ 3 . Near the Fe K-edge, relevant for RXES, same reduction in diamond path length yields a much larger gain of ≈ 13 -15 in photon flux, and thus a correspondingly stronger detectable emission signal, highlighting the importance of suitable diamond choice.

Between the diamonds a rhenium gasket is placed. It functions as a barrier amidst the diamonds protecting them from direct contact, which would lead to destruction. Further, the gasket serves as a sample chamber, with a drilled hole ensuring the sample positioning and containing the pressure transmitting medium. Rhenium is an excellent gasket material since it is one of the densest metals with one of the highest melting points of all stable elements. Beside its strength and hardness, it is still being ductile and is non-toxic [113, 114]. The gasket had an initial thickness of $200\text{ }\mu\text{m}$, which was reduced to approximately $20\text{ }\mu\text{m}$ after pre-indentation. A detailed description of gasket preparations can be found in A.1.2 and a detailed inside side view of a ready to use DAC is shown in Fig. 4.3.

The process of gas loading is essential for providing quasi-hydrostatic conditions with small samples at these high pressures via a pressure transmitting medium. The loading entails filling the sample chamber enclosed by the gasket with a suitable gas up to a pressure of 2000 bar [115]. Generally, pressure transmitting media include, next to the noble gases, salts (e.g. NaCl, KCl) and alcohols. But the properties of noble gases are the best suitable [116], therefore argon was used in this thesis for measuring Fe_2O_3 . Whereas for DACs containing the HBGs, no pressure medium was used. The DACs were fully filled several times with fine grounded powder and compressed after a new filling. A description of the gas loading process is provided in App. A.1.3.

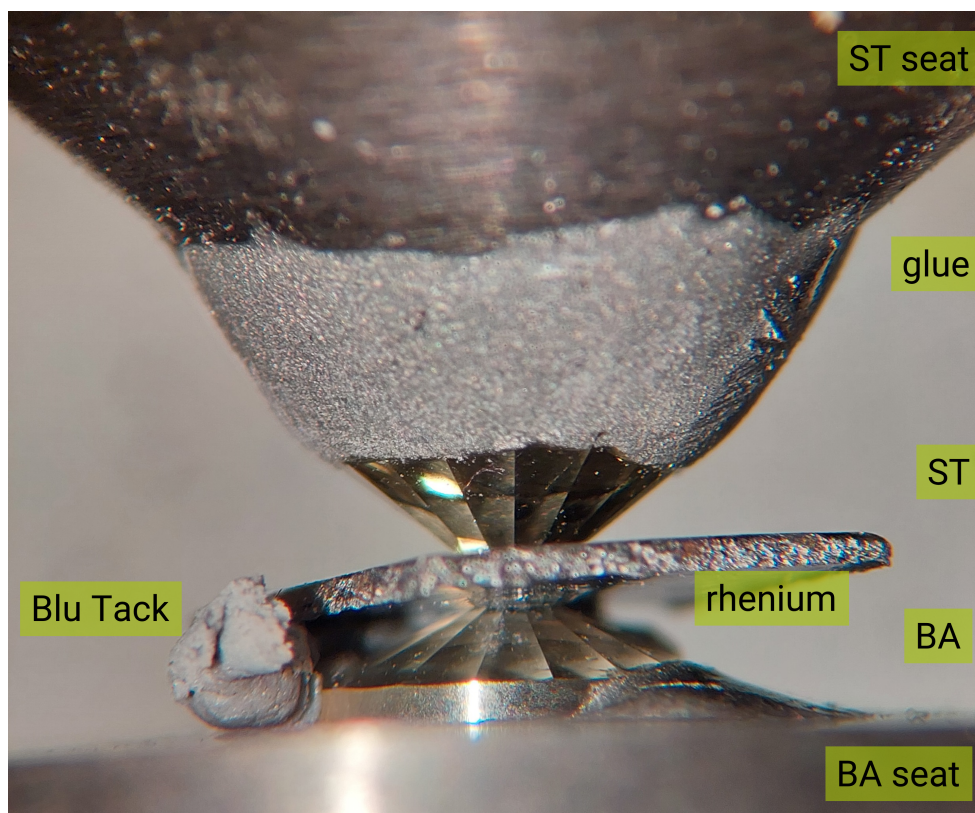


Figure 4.3: Detailed side view photo of an equipped DAC. From top: ST seat with glue holding the ST; rhenium gasket between the ST and BA diamonds containing the sample inside in a hole; Blu Tack holds the rhenium in place during assembly; BA diamond glued to its seat.

4.1.3 Pressure determination

Accurate determination of the pressure inside the DAC, and thus within the sample, is essential for reliable data interpretation. In this thesis, optical Raman spectroscopy was employed as the primary method. For completeness, alternative approaches based on X-ray diffraction and fluorescence spectroscopy are briefly discussed below.

XRD enables pressure determination by placing a marker material inside the sample chamber. Commonly used markers include gold, copper, or aluminum, whose equations of state (EOS) are well established. The positions of the marker's diffraction peaks provide a direct measure of the prevailing pressure [81, 117]. However, this approach requires a dedicated diffraction setup or additional beamtime and was therefore not practical in the context of this work.

Fluorescence spectroscopy offers a comparatively simple implementation, typically by placing $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ (ruby) inside the sample chamber. A laser excites the Cr^{3+} ions, resulting in fluorescence that under hydrostatic conditions yields two sharp emission lines (R1 and R2). The R1 line shifts systematically towards higher energies with increasing pressure, enabling pressure determination via an optical spectrometer. The method, however, has limitations: under non-hydrostatic conditions the R1 and R2 lines broaden and overlap, and at higher pressures the R1 line decreases in intensity, complicating

the analysis and increasing the likelihood of misinterpretation [81, 118–122]. For these reasons, fluorescence spectroscopy was not employed in this thesis.

The method of choice in this work is **optical Raman spectroscopy**, which exploits the shift of the Raman band of the diamond anvils. The high-frequency edge of the diamonds Raman band correlates with stress at the culet and exhibits a linear dependence on pressure up to 30 GPa [123]. At higher pressures, a calibration is required to ensure accuracy. The resulting calibration function is independent of loading conditions, culet size, pressure medium, and gasket material [124, 125].

A widely used calibration was presented by Akahama et al. [125], who reported an accuracy of approximately 3%. It is based on the following relation, valid for quasi-hydrostatic conditions up to 600 GPa, expressed as a function of the relative shift in Raman band frequency [126, 127]:

$$P[\text{GPa}] = K_0 \frac{\Delta\nu}{\nu_0} \left[1 + \frac{1}{2}(K'_0 - 1) \frac{\Delta\nu}{\nu_0} \right] \quad (4.1)$$

where K_0 is the bulk modulus of diamond ($K_0 = 547$ GPa), K'_0 its pressure derivative ($K'_0 = 3.75$), ν_0 the Raman band edge at ambient pressure ($\nu_0 = 1334 \text{ cm}^{-1}$), and $\Delta\nu$ the pressure-induced shift in frequency. An example spectrum recorded at beamline P02

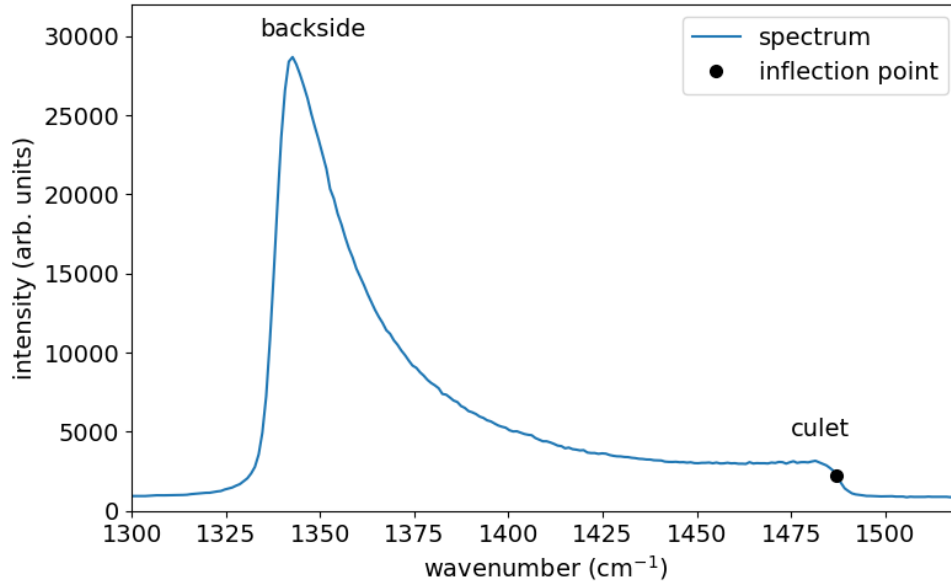


Figure 4.4: Example Raman spectrum of the diamond inside a DAC including the inflection point at the culet marked in black. The inflection point here is at 1487 cm^{-1} corresponding to a pressure of about 73 GPa.

at PETRA III, Deutsches-Elektronen-Synchrotron (DESY) is shown in Fig. 4.4. A laser ($\lambda = 532 \text{ nm}$) excites the diamond and yields a spectrum covering both the backside and the culet. Since the culet is in direct contact with the sample, the laser must be focused onto the center of the culet. The pressure is determined from the inflection point of the slope on the high-frequency side of the Raman band, corresponding to the minimum of the derivative of the spectrum.

For practical purposes, an online calculator¹ was used during experiments to quickly convert the measured Raman shift into pressure values using the Akahama et al. [125] calibration. The pressure determination for Fe₂O₃ was carried out at P02, PETRA III, DESY and for the haplobasaltic glasses at the European Synchrotron Radiation Facility (ESRF). In this thesis, an error of 2 GPa was estimated and will be used throughout.

4.2 Haplobasaltic glass synthesizing and characterization

Synthesizing

The HBGs are simplified basaltic compositions synthesized under controlled laboratory conditions. The glass samples used in this work were produced in collaboration with Prof. Dr. Sindy Fuhrmann at TU Bergakademie Freiberg with assistance from Lena Bussmann, and subsequently reduced in cooperation with Prof. Dr. Max Wilke and Thomas Block at the University of Potsdam. Redox treatment of the HBG resulted in samples with different Fe^{3+}/Fe_{tot} ratios, which were later pressurized up to 120 GPa. The complete workflow, including synthesis, redox treatment, and characterization, is described in this chapter

The initial synthesis of the starting material, the base HBG composition, was performed in Freiberg. The mineral composition is listed in Tab. 4.1, the isotope ⁵⁷Fe was incorporated to enable SMS measurements. A heat-resistant corundum crucible was pre-heated in a muffle furnace at 1100 °C for approximately 30 minutes. The powdered minerals were weighed, mixed, and transferred into the crucible, which was then placed in a furnace at 1450 °C for one hour to melt the mixture under an oxygen atmosphere.

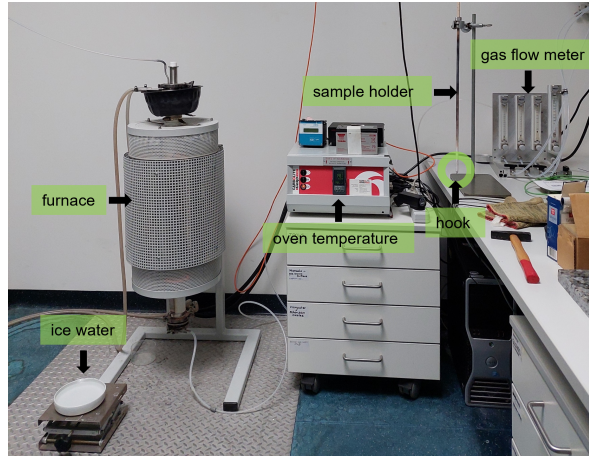
The resulting melt was quenched by pouring it onto a steel plate; the rapid cooling prevented crystallization and produced a glass. To relieve internal stresses and improve mechanical stability, the quenched glass was annealed overnight at 730 °C, yielding the base haplobasaltic glass used in this study. Additionally, two more HBG compositions

Table 4.1: Chemical composition of starting material for synthesis of the base haplobasaltic glass.

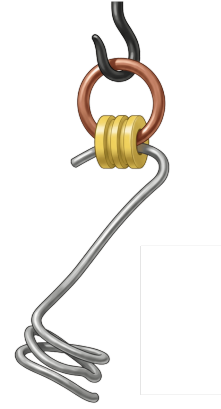
component	wt%	mol%
SiO ₂	49	50.3
CaO	19	20.9
Al ₂ O ₃	16	9.7
MgO	8	12.2
FeO	8	6.9

with different Fe^{3+}/Fe_{tot} ratios were produced by reducing the base glass. Redox treatment was carried out using a small laboratory furnace (Fig. 4.5a). The samples were not held in a crucible; instead, small pieces of base HBG were mounted on a platinum wire (Fig. 4.5b). Platinum was chosen after rhenium wires were tested and found unsuitable, as glass quenched from rhenium wires consistently crystallized regardless of quenching technique. This crystallization did not occur when using saturated platinum wires.

¹<http://kantord.50webs.com/ruby.htm>



(a) Setup with a small furnace. The sample holder is inserted into the furnace, and the platinum wire (right) is mounted below the corundum insulator. The furnace atmosphere is controlled with a gas flow meter. Samples are quenched in ice-salt water.



(b) Sketch of the platinum wire used for redox treatment. The glass piece is placed on the wire (silver) and fixed with glue. Corundum rings (yellow) isolate the wire from a hoop (copper) from the sample holder (black) which is in the oven. The size as a whole is roughly 3 to 4 cm. Improved with AI [35].

Figure 4.5: Setup in Potsdam for reducing the base haplobasaltic glass to obtain additional compositions with different Fe^{3+}/Fe_{tot} ratio.

The procedure for reducing the glass was the following:

1. A small loop of platinum wire has to be formed (see 4.5b).
2. Performing a saturation step: a small piece of glass (not used afterward) has to be attached to the wire using the same procedure as steps 3-10, but heating it only for 30 minutes in air. This prevents uncontrolled reactions between glass and platinum during later reduction. If a new wire is used, this saturation must be repeated. The glass used for the saturation process should be disposed.
3. On the saturated platinum wire the base glass with about 100 mg is placed and fixated by a Muviol or Mowinol²-H₂O solution and must harden.
4. Before placing the platinum wire onto the sample holder, 4 corundum isolators on a thin metal wire are placed in between. This prevents heating of the platinum wire and therefore the sample through thermal conduction with the sample holder.
5. The oven temperature was set to 1470 °C, which corresponds to around 1310 °C inside the oven. This temperature measurement on the sample is disrupted by the furnace. The temperature was measured when the furnace was switched off. After switching off, the temperature jumps to the true value. This is consistent with the furnace calibration.
6. Then the gas flow of N₂H₂ and CO₂ can be adjusted at the flow meter. For achieving an equilibrium, a short wait of a few minutes is sufficient.
7. When placing the sample holder into the furnace, the white plug has to be removed first. For around one hour the sample stays in the furnace.
8. The bowl containing the ice water mixed with salt is placed under the oven and raised high enough so that the collection container emerges it. After a short wait

²polyvinyl alcohol

- until the collection container has cooled down, the sample can be dropped.
9. To drop the glass sample including the platinum wire, the cables attached at the top are connected to a battery, which causes the thin metal wire to melt.
 10. For checking whether the sample is still attached to the thin metal wire, the ohmmeter can be used.

Characterization

An initial assessment of crystallization was performed using a **polarization microscope**. The redox-treated HBG samples were placed on a glass slide and examined between crossed polarizers. Under these conditions, isotropic (non-crystalline) glass appears dark, whereas crystalline phases show bright interference spots. By rotating the stage, the optical behavior of individual grains could be assessed, allowing distinction between amorphous and crystalline regions. If bright crystalline areas are visible, the sample is considered unsuitable [128, 129].

Table 4.2: Experimental conditions, averaged chemical compositions from EPMA analysis and WCCA results for the HBG samples.

glass		1	2	3
conditions ³	production name	HB_JFe57	HB_JFe57_3CO2	HB_JFe57_2
	temperature furnace (°C)	1450	1470	1470
	temperature sample (°C)	1450	1360	1360
	CO ₂ (l/min)	-	0.2	0.1
	N ₂ H ₂ (l/min) (5% H ₂)	-	-	0.6
	time in furnace (min)	60	90	30
EPMA ⁴	SiO ₂ (wt%)	44.300	45.551	46.214
	CaO (wt%)	16.634	17.410	17.346
	Al ₂ O ₃ (wt%)	26.376	23.595	24.021
	MgO (wt%)	6.619	6.820	6.841
	FeO (wt%)	6.711	6.903	6.346
	TiO ₂ (wt%)	0.160	0.165	0.161
	Na ₂ O (wt%)	0.071	0.065	0.095
	K ₂ O (wt%)	0.077	0.017	0.092
	MnO (wt%)	0.008	0.007	0.006
wc ⁵	FeO (wt%)	6.99	6.82	6.72
	Fe ³⁺ /Fe _{tot} (wt%)	61	47	13

First elemental analyses of the glass samples were conducted in Potsdam using **energy-dispersive X-ray spectroscopy (EDX)** attached to a scanning electron microscope (SEM). The samples were mounted on stubs and coated with a thin conductive carbon

³production conditions

⁴averaged results

⁵wet chemical colorimetric results

layer to minimize charging effects. Characteristic X-rays emitted from the sample surface were detected and used to determine the elemental composition. The obtained spectra allowed qualitative identification of elements, providing insights into compositional variations. In contrast to the following mentioned electron probe microanalysis (EPMA), EDX is not able to detect low abundance elements below 0.2 wt% [130].

For precise quantitative analysis, an in depth elemental distribution analysis was conducted by the group of Prof. Dr. Harald Behrens from the Leibniz University Hannover by using **EPMA**. This method enables precise quantitative determination of elemental concentrations by measuring characteristic X-ray emissions generated by a focused electron beam. The technique provides high spatial resolution and allows differentiation between glassy and crystalline regions based on compositional contrast. The obtained data were used to confirm elemental distributions. The results of the full analysis is given in the Appendix A.3 [131]. As EPMA solely provides total Fe amount, it cannot distinguish Fe^{2+} and Fe^{3+} .

In addition, **wet-chemical colorimetric analysis (WCCA)** was performed by the group of Dr. Harald Behrens to determine the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio. This analytical technique is used to determine the concentration of specific elements or compounds in a solution through color-producing chemical reactions. A reagent is added to the sample to form a colored complex, and the intensity of the resulting color is directly related to the analyte concentration according to the Lambert-Beer law, which states that absorbance is proportional to the concentration of the absorbing species and the optical path length. The absorbance is typically measured using a spectrophotometer or photometer at a defined wavelength. This method enables the determination of the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio. The used method for the analysis is based on Schuessler et al. [132].

A table containing the three HBG composition with their respective synthesizing conditions as well as their averaged elemental distribution from EPMA and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio from WCCA are listed in Tab. 4.2.

4.3 Von Hámos spectrometer

The von Hámos spectrometer is a wavelength-dispersive X-ray spectrometer that employs cylindrically curved analyzer crystals to disperse and focus X-rays on a 2D area detector. This type of spectrometer relies on the von Hámos geometry, where both the photon-emitting sample and the detector are positioned along the focal circle of the curved analyzer crystal [133]. X-rays emitted from the sample are diffracted by the analyzer crystal according to Bragg's law (cf. Eq. 3.4) and are spatially separated by wavelength along the detector plane. This configuration enables high spectral resolution and allows simultaneous detection of a broad energy range without mechanical scanning of crystals and detector.

Depending on the desired measurement, the analyzer crystal's material and miller indices have to be chosen and the geometry, e.g. the detector height, has to be adjusted accordingly. A useful tool for planning the experiment for transition metals is the website provided by Dr. Florian Otte ⁶ [134]. An example for finding the right analyzer crystal, their Miller indices and the corresponding detector height is given below.

⁶<http://www.where-are-my-photons.com/>

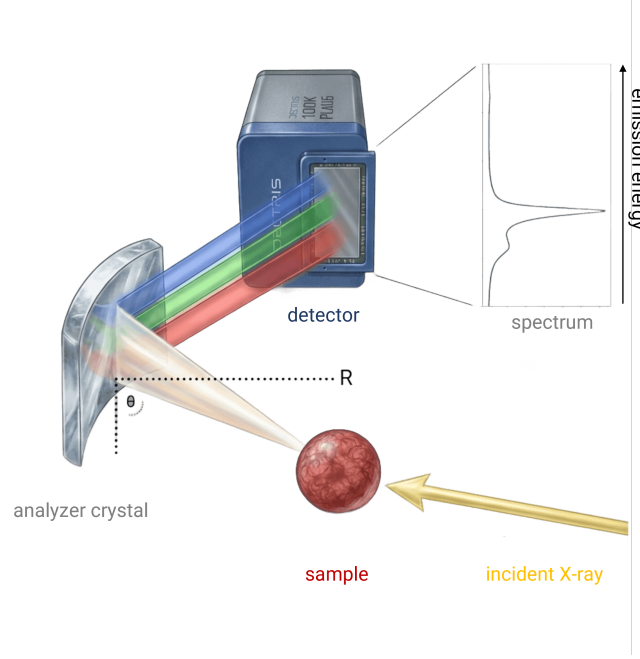


Figure 4.6: Schematic representation of the von Hámos geometry. X-rays emitted from the sample are diffracted by the cylindrically curved analyzer crystal and horizontally focused while wavelength-dispersively projected onto an area detector, producing an emission spectrum after data processing. Improved with AI [35].

For measuring the $K\beta$ emission line at 7058 eV [135] a conversion to a wavelength in Ångström is necessary via the Planck relation

$$\lambda = hc/E \approx 1.756 \text{ Å} \quad (4.2)$$

with λ as the wavelength, h as Planck constant and c is the speed of light. The Bragg's law (Eq. 3.4) with d , the interplanar spacing, the Miller indices hkl and the Bragg angle $\sin(\Theta)$ is transposed to

$$d_{hkl} = \lambda / 2\sin(\Theta). \quad (4.3)$$

With a desired Bragg angle of about 60° , the spacing is

$$d \approx 1.756 \text{ Å} / 2\sin(66^\circ) \approx 1.014 \text{ Å}. \quad (4.4)$$

This d-spacing can be compared to potential analyzer crystal materials like for example Si(110) and their higher order reflection. For example the d-spacing of Si(440) is $d_{hkl} = a / \sqrt{h^2 + k^2 + l^2} = 0.960 \text{ Å}$ [136] with the lattice parameter $a = 5.431 \text{ Å}$ for silicon [137] and $h = 4$, $k = 4$, $l = 0$ for the plane. Although this is not an exact match, adjusting the Bragg angle slightly to 66° yields a suitable configuration. Because the sample height is fixed by the incident X-ray beam position, the height of the analyzer crystals and the detector relative to the sample must be calculated using:

$$z_{\text{analyzer}} = R \cdot \cot(\Theta) \quad \text{and} \quad z_{\text{detector}} = 2R \cdot \cot(\Theta) \quad (4.5)$$

with $R = 500 \text{ mm}$ bending radius of the crystals, the analyzer crystals' height results in $z_{\text{analyzer}} \approx 220 \text{ mm}$ and for the detector in $z_{\text{detector}} \approx 440 \text{ mm}$.

In order to minimize absorption of the incident X-ray beam due to the diamond and maximize the emitted signal, a dedicated **scattering geometry** was employed. This geometry has been described in detail by Dr. Christian Thiering (né Albers) [115]. For clarity, only a condensed description is given here, and a schematic of the setup is shown in Fig. 4.7. In this configuration, the ST diamond is placed downstream, while the BA

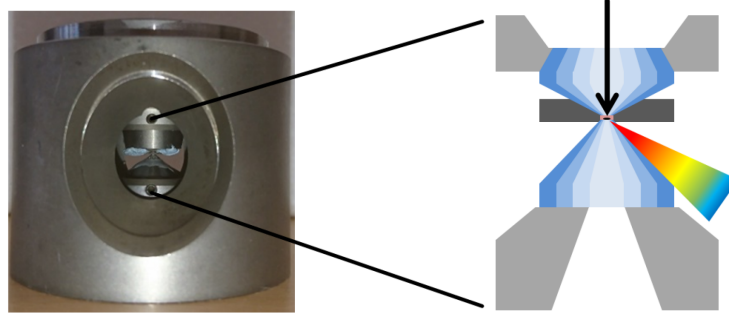


Figure 4.7: (left) side view photograph of an equipped BX90-RD (right) sketch of the scattering geometry with a $\sim 70^\circ$ scattering angle. Reproduced with permission from Dr. Christian Thiering, né Albers [115].

or, preferably, the MD diamond is positioned upstream. This arrangement is combined with a scattering angle of 70° and a specific gasket indentation process (see Section A.1.2).

The choice of a 70° scattering angle provides a main advantages, it minimizes background scattering from the diamonds, ensuring that only photons originating from or near the sample are detected. Together with earlier mentioned choice of DAC, diamonds, their seats and gasket flip, these improvements make it possible to perform RXES measurements at very high resolution within reasonable measurement times. Further details on the RXES setup at beamline P01 are provided in Section 4.4.

The von Hámos spectrometer further enables **two-color experiments**, which allow the simultaneous measurement of two different emission lines. Namely, the $K\alpha$ and $K\beta$ emission line can be captured at the same time, when employing two different analyzer crystals, the Si(111) and Si(110), respectively. This is due to the similar geometrical requirements to set proper energy detection windows of the above-mentioned emission lines resulting in a detector height difference of about 4 mm [115]. Advantage of this technique is the time efficiency of simultaneous monitoring of valence- and core-level transitions.

4.4 Beamline setup P01

The (R)XES measurements for Fe_2O_3 were conducted at beamline P01, PETRA III at DESY. PETRA III is one of the most brilliant storage-ring-based X-ray radiation sources worldwide, operating at 6 GeV particle energy and up to 120 mA beam current [138]. The beamline P01 is specialized in (resonant) inelastic X-ray scattering (and resonant nuclear scattering), offering a broad energy range between 2.5 to 74 keV as well as a beam size on the sample as small as $4 \times 7 \mu\text{m}^2$. The maximum flux on the sample is up to 7×10^{13} photons/s at 14.4 keV [139, 140]. These characteristics make P01

ideally suited for high resolution (R)XES experiments. Furthermore, both the portable laser-heating system [141] and the portable von Hámos spectrometer (equipped with a Pilatus 100K area detector) are designed for use at P01. Over the past years this setup was successfully applied in numerous studies [115, 141–147].

A schematic overview of the setup at P01 is shown in Fig. 4.8 left). The portable **laser-heating system** [141] consists of a 100 W double-sided Yb:YAG fiber-laser with a wavelength of 1070 nm. The laser beam is first divided into two branches by a polarizing beam splitter to enable double-sided operation. The intensity of each branch is then controlled independently by a motorized phase-shifting plate positioned upstream of a second polarizing beam splitter; depending on the applied phase shift, part of the beam is transmitted while the remaining fraction is diverted into a metal block acting as a beam dump. After intensity adjustment, both beams are routed toward the sample such that they intersect it at a 90° angle relative to the incident X-rays. The upstream and downstream beam paths follow opposite sequences of focusing and redirection: on the upstream side the collimated beam is first focused and then redirected by a mirror so that it is aligned coaxially with the X-ray beam. On the downstream side the order is reversed. The beam is first reflected by a mirror into the X-ray axis and only then focused onto the sample. The upstream mirror contains a $300\text{ }\mu\text{m}$ aperture that allows the incident X-rays to pass through without measurable attenuation. Motorized mirror stages on both sides permit fine alignment to ensure that the two laser beams meet the sample in a symmetric and spatially overlapping manner during double-sided heating.

Temperature measurements were performed by collecting the thermal emission of the sample via black body radiation and fitting the spectra with a Planck function, a detailed description can be found in Chapter 5.3.

The von Hámos spectrometer (cf. Fig. 4.8 right)) on its custom-built mount [148] with the Pilatus 100K detector can be implemented above the laser-heating setup. A helium filled thin plastic bag (trash bag) is placed between the sample, von Hámos spectrometer and detector for reducing the air scattering and thereby increasing the detected intensity of the emission (signal-to-noise ratio) by a factor ≈ 5 [115]. For the measurements the Si(111) monochromator was used, and the beam was focused to about $7 \times 7\text{ }\mu\text{m}^2$. Depending on the measurements, the energy varied between 7000 eV and 10400 eV. The analyzer crystals have a height of 32 mm and a bending radius of 500 mm. RXES was performed with Si(111) crystals using the Si(333) reflection. For XES Si(110) crystals were used with the Si(440) reflection, and the Si(660) reflection was used for measuring the elastic scattering for energy calibration (further elaborated in 5.4). Pictures from the experimental setup are shown in App. A.6.1.

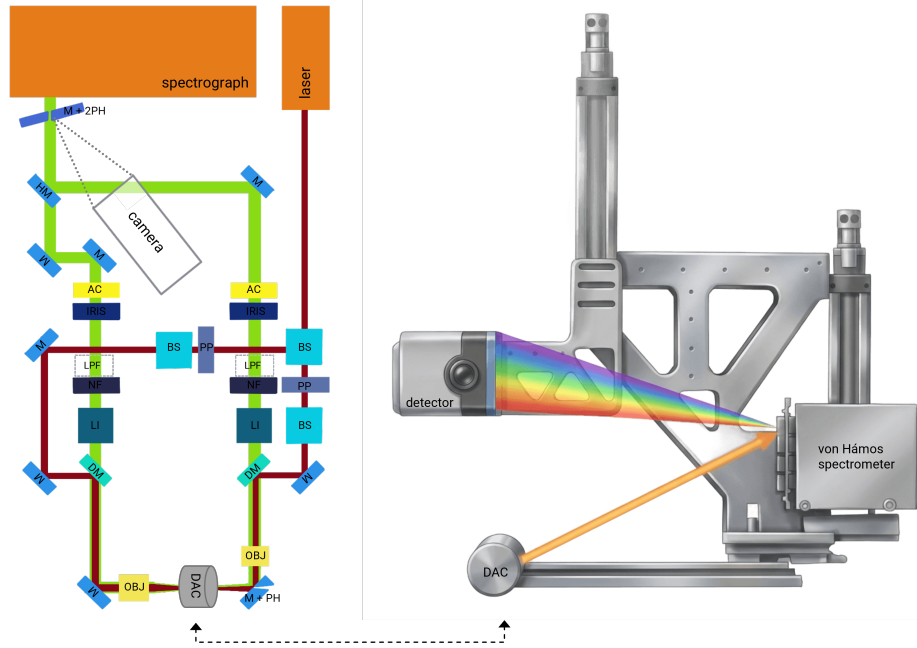


Figure 4.8: Schematic overview of the experimental setup at beamline P01, PETRA III, DESY including: **left**) laser-heating system top-view scheme (objective (OBJ), achromat lens (AC), mirror (M), half-mirror (HM), pinhole (PH), dichroic mirror (DM), beam splitter (BS), white light source (LI), phase-shifting plate (PP), notch filter (NF), long pass filter (LPF)) (redrawn after Spiekermann et al. [141], licensed under CC BY) and **right**) Schematic image of the von Hámoss spectrometer including the Pilatus 100K area detector (modified after [148] and improved with AI [35]). The helium filled bag between the sample, detector and spectrometer is not shown. The DAC is shown from its backside.

4.5 Beamline setup ID20

The experimental study of the iron-bearing haplobasaltic glasses at high pressure was conducted at the ESRF, the world's brightest synchrotron light source in Grenoble, France [149].

Beamline ID20 is dedicated to resonant and non-resonant inelastic X-ray scattering, covering an energy range between 4 and 20 keV with a beam focus down to $7 \times 9 \mu\text{m}^2$. Due to the implemented von Hámoss spectrometer, ID20 offers excellent conditions for X-ray emission spectroscopy on iron-bearing materials [150, 151]. The von Hámoss spectrometer at ID20 is equipped with three analyzer crystals. During the first beamtime, two Si(110) analyzers were used for XES and one Si(111) analyzer for RXES. During the second beamtime, all three analyzers were Si(111) crystals, used for XES. The bending radius of the crystals is 250 mm and they are mounted inside a vacuum chamber. A Maxipix hybrid pixel detector (5×1) is positioned above the sample (cf. Fig. 4.9) [150]. Pictures from the experimental setup are shown in App. A.6.2. The average measurement time was 30 Minutes per sample and pressure point.

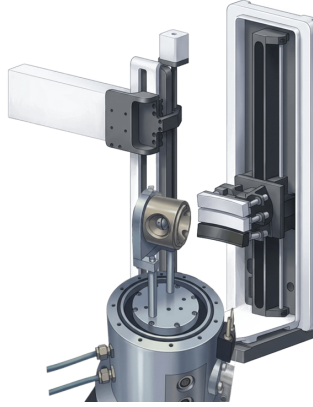


Figure 4.9: Scheme of the von Hámós spectrometer setup at ID20 (ESRF), where the vacuum chamber around the von Hámós is not visible for illustration purposes (von Hámós spectrometer redrawn after Sahle et al. [150], licensed under CC BY, and improved with AI [35]).

4.6 Beamline setup ID18

Beamline ID18 was the dedicated SMS beamline at ESRF, which is now located at ID14. ID18 operated using the nuclear Bragg reflections of iron borate ($^{57}\text{FeBO}_3$), providing ^{57}Fe resonant, polarized X-ray radiation at 14.4 keV with a bandwidth of approximately 15 neV and tunability of $\pm 0.6 \mu\text{eV}$. In contrast to conventional radioactive sources, this provides a beam with high photon flux on a small focus ($10 \times 5 \mu\text{m}^2$ on the sample), enabling measurements on very small samples or in extreme conditions such as high pressure and high/low temperature [94]. A simplified scheme of ID18 is shown in Fig. 4.10. The X-ray beam is monochromatized by a high-heat-load monochromator (mono), resulting in a bandwidth of $\approx 15 \text{ meV}$. The deflector (def) diverts the beam onto the iron borate crystal (IB). The IB finalizes the monochromatization to around 10 neV. Afterward, Kirkpatrick-Baez (KB) mirror focuses the SMS beam onto the sample in the DAC and through onto a avalanche photodiode detector [94]. SMS enables

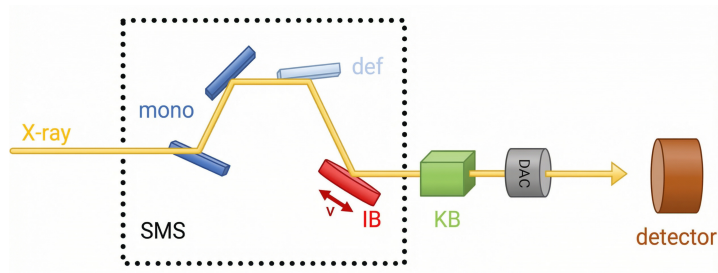


Figure 4.10: Simplified scheme of ID18 where, **mono** denotes a monochromator, **def** stands for deflector, **IB** is the iron borate crystal, which moves with the velocity **v**. **KB** is the Kirkpatrick-Baez mirror (modified after [94] and improved with AI [35]).

determination of the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio and provides element-specific information on electronic and magnetic states. The calibrations were done via $\alpha\text{-Fe}$ and the velocity scale was between -8 and 8 mm/s . Measurement times were between around 24 up to 200 minutes, with a roughly average time of 96 minutes.

5 Electronic and structural evolution of Fe_2O_3 at conditions of the Earth's mantle – Formation of higher iron oxides

5.1 Scientific background

Fe_2O_3 may influence physical properties, redox equilibria, and magnetic behavior in the deep Earth [11, 152]. It has emerged as a particularly complex system under compression, exhibiting multiple pressure- and temperature-induced structural and electronic transformations [11, 41, 49, 51, 152–159]. To place the present study in context, the following section reviews key experimental and theoretical investigations of Fe_2O_3 under HP/HT conditions.

The pressure-induced transformation of Fe_2O_3 was first identified in early synchrotron XRD experiments performed under ambient-temperature compression. Staun Olsen et al. (1991) [153] observed the appearance of a new high-pressure phase between 50 and 60 GPa, with diffraction peaks of the high-pressure phase beginning to emerge near 50 GPa and the transformation being nearly complete by 60 GPa. This structural change was accompanied by a volume collapse of approximately 10%. Based on diffraction data alone, the transition was interpreted as a transformation from the $\alpha\text{-Fe}_2\text{O}_3$ corundum structure ($R\bar{3}c$) to an orthorhombic perovskite-type structure.

A significant advance was made by Pasternak et al. (1999) [154], who combined Mössbauer spectroscopy, XRD, and electrical resistance measurements to investigate Fe_2O_3 up to 80 GPa at ambient temperature and down to 4 K. These authors identified a broad pressure interval between approximately 42 and 58 GPa magnetic and isolating phases coexist, followed by the stabilization of a fully nonmagnetic high-pressure phase above ≈ 72 GPa. Structurally, the high-pressure phase was assigned to a distorted corundum ($\text{Rh}_2\text{O}_3(\text{II})$ -type, Pbcn) structure with sixfold coordinated iron and a volume collapse of approximately 10%, demonstrating that coordination increase is not required to produce the observed densification. The collapse of magnetism was interpreted as evidence for electronic delocalization and a breakdown of d - d correlations.

The crystallographic interpretation of the pressure-induced transition was refined later by Rozenberg et al. (2002) [155] using detailed XRD refinements supported by *ab initio* calculations. These authors confirmed that the high-pressure phase is best described as a $\text{Rh}_2\text{O}_3(\text{II})$ -type structure, with iron remaining sixfold coordinated, and explicitly ruled out perovskite-type models. The large volume collapse observed at the transition pressure was thus attributed primarily to electronic effects rather than changes in coordination geometry. In this work, changes in spin-state were inferred from previously published Mössbauer and transport data rather than measured directly, and experiments were restricted to ambient temperature.

The influence of temperature on phase transformations in Fe_2O_3 was highlighted by laser-heating studies. Liu et al. (2003) [156] showed that under ambient temperature compression the transition to the $\text{Rh}_2\text{O}_3(\text{II})$ -type phase begins near 45-50 GPa, whereas laser heating to temperatures up to ≈ 3500 K can induce structural changes at significantly lower pressures, including the appearance of an additional orthorhombic phase at 22 GPa whose structure was not fully determined.

Systematic high-pressure/high-temperature diffraction studies were conducted by Ono et al. (2004) [49]. They reported that laser heating to ≈ 2700 K induces a transformation from hematite (corundum structure) to an orthorhombic perovskite-type structure at pressures near 30 GPa, and further heating at pressures approaching 70 GPa produces a post-perovskite-type phase [49]. Subsequent work by Ono and Ohishi (2005) [157] mapped the phase relations over a wider pressure-temperature range and identified two distinct HP phases: an intermediate $\text{Rh}_2\text{O}_3(\text{II})$ -type phase (HP1) stabilized between ≈ 55 and 58 GPa at temperatures between 1220 and 1990 K, and a CaIrO_3 -type post-perovskite phase (HP2) stabilized above ≈ 60 -65 GPa at temperatures exceeding ≈ 1600 K [157]. The post-perovskite structure was reported to contain two crystallographically distinct iron sites with sixfold and eightfold coordination.

Direct evidence that structural and electronic responses can be decoupled in Fe_2O_3 was provided by Badro et al. (2002), who combined XES with XRD at HP [41]. In their experiments, laser heating at 46 GPa drove Fe_2O_3 into a HP crystal structure and an LS state, as indicated by a collapse of the magnetic moment. Upon subsequent relaxation at constant pressure and room temperature, the spin-state reverted toward HS while the HP structure persisted, demonstrating that spin-state and crystallographic structure are not uniquely linked and that metastable combinations of the two can exist under non-equilibrium conditions.

Local structure sensitive measurements further constrained the sequence of electronic and structural changes. Sanson et al. (2016) [158] combined Fe K-edge EXAFS and XANES measurements under ambient-temperature compression and observed an abrupt shortening of Fe-O bond lengths and a reduction in octahedral distortion near 50 GPa. Analysis of the XANES pre-edge indicated a HS to LS crossover between approximately 50 and 55 GPa, with the electronic transition progressing more rapidly than the structural transformation. These results suggested that the electronic transition precedes and potentially drives the structural collapse under room-temperature conditions in contradiction to the findings of Badro et al [41].

HP/HT equilibrium behavior was addressed using combined XRD and SMS as well as *ab initio* calculations by Shim et al. (2009) [152]. They demonstrated that hematite remains stable up to ≈ 55 GPa at ambient temperature, transforms to a nonmagnetic $\text{Rh}_2\text{O}_3(\text{II})$ -type phase up to 70 GPa, and converts to a post-perovskite phase only after laser heating to temperatures of about 2000 K. In the post-perovskite phase, at least half of the Fe^{3+} ions were reported to adopt a HS configuration on distinct octahedral and biprismatic sites, indicating a recovery of magnetism associated with the structural transition.

Multi-anvil experiments provided additional constraints on the role of temperature and kinetics. Ito et al. (2009) [51] found that hematite remains stable to at least 58 GPa under ambient temperature compression, whereas heating above ≈ 500 K induces

a transformation to a $\text{Rh}_2\text{O}_3(\text{II})$ -type phase between 32 and 44 GPa, followed by the appearance of a further orthorhombic phase at higher pressures and temperatures.

A comprehensive view of Fe_2O_3 polymorphism and electronic behavior was provided by Bykova et al. (2016) [11] through combined single-crystal XRD and SMS up to pressures of 113 GPa and temperatures of approximately 3000 K. These authors identified a sequence of pressure-induced phases, including ζ (distorted perovskite)- and θ (orthorhombic)- Fe_2O_3 as well as temperature-induced phases ι ($\text{Rh}_2\text{O}_3(\text{II})$)- and η (post-perovskite)- Fe_2O_3 . Further they demonstrated a non-monotonic evolution of the iron spin-state, with transitions from HS to mixed-spin, to LS. At the highest temperatures, partial decomposition into mixed-valence higher iron oxides was observed. A modified version of their phase diagram can be seen in Fig. 5.1. Moreover, they found above 60 GPa and 2000 K the higher oxides Fe_5O_7 and $\text{Fe}_{25}\text{O}_{32}$ after heating Fe_2O_3 and Fe_3O_4 , respectively. A pathway forming Fe_3O_4 from Fe_2O_3 is possible under reducing conditions and elevated temperatures [160].

Additional experimental and theoretical studies further emphasized the complexity of the electronic transition. Greenberg et al. (2018) [159] combined Mössbauer spectroscopy, XRD, and *ab initio* calculations to show that metallization in Fe_2O_3 proceeds via a site-selective Mott transition, with electrons delocalizing on only a subset of iron sites across multiple structural phases under room-temperature compression. Recent high-resolution (R)XES measurements by Albers et al. (2023) [161] demonstrated that Fe $K\beta$ emission features remain sensitive to pressure-induced spin-state changes up to at least 75 GPa at ambient temperature, revealing a two-step reduction of the spin moment rather.

In addition to static compression experiments, Fe_2O_3 has also been investigated using shock-compression techniques, which access substantially LS on very short timescales; however, the transient nature of these experiments and the associated non-equilibrium conditions limit their direct applicability to the present study, which focuses on quasi-equilibrium behavior under static HP/HT conditions [162–165]. In stark contrast to findings in static compression experiments, they found an isostructural phase transition from α to α' , highlighting the different pathways [165].

While these studies have significantly advanced the understanding of Fe_2O_3 under compression, they also reveal substantial discrepancies arising from differences in temperature conditions, kinetic effects, and experimental probes. Taken together, these studies demonstrate that the behavior of Fe_2O_3 at HP is governed by a complex interplay of structural transformations, electronic transitions, temperature effects, and kinetic constraints. Kinetic constraints arise from the fact that phase transitions, especially reconstructive structural transformations, involve bond breaking, coordination changes, and long-range atomic rearrangements. These processes require thermal activation. At HP but low temperature, diffusion is limited, so the system can remain trapped in metastable configurations even if another phase is thermodynamically favored.

Despite extensive investigation, systematic electronic-structure measurements under simultaneous HP/HT remain limited. Understanding its behavior under conditions relevant to the Earth's adiabatic temperature profile [10] therefore requires experimental approaches that simultaneously probe crystal structure and electronic state at high pressure and temperature.

This gap provides strong motivation for experimental approaches that combine HP laser heating with complementary probing of both crystal structure and electronic state. In this context, XRD provides direct identification of pressure and temperature dependent phase relations, while XES and RXES offer sensitivity to changes in the Fe spin-state under *in situ* conditions. The combined application of XES, RXES, and XRD is therefore essential for resolving the electronic and structural evolution of Fe_2O_3 along adiabatic temperature profile relevant pressure and temperature paths [10].

Given its comprehensive treatment of Fe_2O_3 polymorphism under HP/HT conditions, the phase stability diagram reported by Bykova et al. [11] is used as a reference framework for the present study (cf. Fig. 5.1). Based on this diagram, laser-heating experiments were conducted at pressures of 38, 64, and 80 GPa, corresponding to distinct stability fields along the Earth's adiabatic temperature profile [10]. At each pressure, XES and RXES data were collected, with subsequent phase verification performed using XRD.

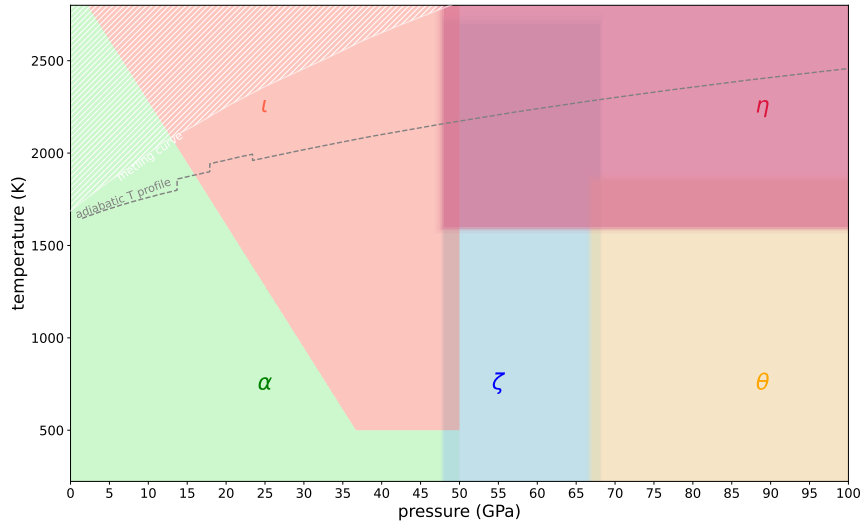


Figure 5.1: Phase stability fields of Fe_2O_3 with pressure and temperature conditions, modified after Bykova et al. [11] with an adapted boundary between α - and ι - Fe_2O_3 from Ito et al. [51]. The Earth's adiabatic temperature profile is based on Katsura et al. [10] and the FeO melting curve is a proxy from Morard et al. [166]. Region for ζ - Fe_2O_3 is adapted after Albers et al. [161].

5.2 Crystal structures

In order to interpret the pressure- and temperature-induced phase transformations of Fe_2O_3 investigated in this chapter, a brief overview of the crystallographic concepts relevant to the present study is provided. This section introduces lattice systems and space-group symmetry as they pertain specifically to the Fe_2O_3 polymorphs discussed below and serves as a reference framework for the interpretation of XRD data. This section follows Cullity and Stock [167] and Müller [168], for crystal symmetries, based on the crystal structures provided by Bykova et al. [11].

Lattice systems

The crystal structures of Fe_2O_3 relevant to high-pressure and high-temperature conditions belong predominantly to the rhombohedral, orthorhombic, monoclinic, and, in some cases, triclinic lattice systems. These lattice systems are defined by their axial relationships and interaxial angles and reflect different degrees of structural symmetry. Hematite, the ambient-pressure polymorph of Fe_2O_3 , crystallizes in a trigonal setting, whereas several high-pressure polymorphs adopt different symmetries. An overview of the relevant lattice systems is shown in Tab. 5.1.

Table 5.1: Lattice parameter for selected crystal systems extracted from Cullity and Stock [167] with rhombohedral as part of the trigonal system.

crystal system	axial lengths	angles
orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$

Under compression, reductions in symmetry are commonly observed as a response to increasing lattice distortion and changes in bonding geometry. Such symmetry lowering is reflected in the transition to orthorhombic or monoclinic lattice systems and has direct consequences for diffraction peak multiplicity, peak splitting, and the number of crystallographically distinct atomic sites [11].

While lattice systems describe the metric symmetry of the unit cell, the full crystallographic symmetry of a structure is defined by its space group. Space groups combine the underlying Bravais lattice with symmetry operations such as rotations, mirror planes, inversion centers, and glide planes. In the following, the meaning of space-group symbols relevant to Fe_2O_3 polymorphs is briefly summarized to facilitate interpretation of the structural descriptions used throughout this chapter.

Space-group notation

Space-group symbols described by the Hermann-Mauguin notation consist of a lattice-centering symbol followed by symmetry elements that describe rotational, mirror, and glide-plane symmetries. The first letter denotes the Bravais lattice centering, while the subsequent symbols specify symmetry operations along crystallographic directions. An overview of the structures described below is depicted in Fig. 5.2. The following resolved structures are based on Bykova et al. [11].

The space group $R\bar{3}c$, which describes the crystal structure of hematite ($\alpha\text{-Fe}_2\text{O}_3$), belongs to the rhombohedral lattice system. The letter R denotes rhombohedral lattice centering. The symbol $\bar{3}$ indicates a threefold rotoinversion axis, combining a threefold rotation with inversion symmetry. The letter c denotes a glide plane with translation parallel to the crystallographic c axis. Together, these symmetry elements define a structure with a single crystallographic iron site in octahedral coordination.

The orthorhombic space group $Pbcn$, associated with $\iota\text{-Fe}_2\text{O}_3$ consists of a primitive lattice (P) combined with glide planes and mirror symmetries. The letters b and c denote glide planes with translations along the b and c directions, respectively, while n indicates a diagonal glide plane. This space group is commonly associated with

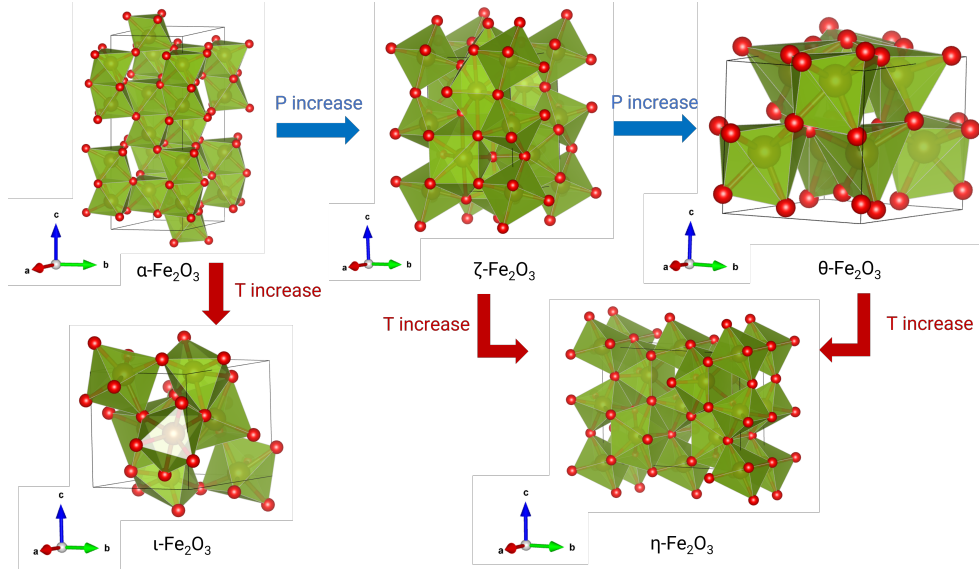


Figure 5.2: Overview of the crystals structures of the Fe_2O_3 phases based on the findings of Bykova et al. [11]. Starting with the $\alpha\text{-Fe}_2\text{O}_3$ phase with $R\bar{3}c$ space group, an increase in temperature results in the $\iota\text{-Fe}_2\text{O}_3$ phase with $Pbcn$, $\text{Rh}_2\text{O}_3(\text{II})$ -type symmetry. When increasing pressure instead of temperature the distorted-perovskite like $\zeta\text{-Fe}_2\text{O}_3$ phase follows with $P\bar{1}$ symmetry and at even higher pressures the structure changes into the $\theta\text{-Fe}_2\text{O}_3$ phase, namely $Aba2$ or $Aea2$ structure. Increasing temperature from $\zeta\text{-Fe}_2\text{O}_3$ and $\theta\text{-Fe}_2\text{O}_3$ phase, the polymorph $\eta\text{-Fe}_2\text{O}_3$ with a post-perovskite-type phase with the space group $Cmcm$ forms.

$\text{Rh}_2\text{O}_3(\text{II})$ -type structures, in which iron remains sixfold coordinated but occupies a lower-symmetry environment compared to $\alpha\text{-Fe}_2\text{O}_3$. The space group $P\bar{1}$ or distorted-perovskite represents the lowest possible crystallographic symmetry and describes the $\zeta\text{-Fe}_2\text{O}_3$ phase. The letter P denotes a primitive lattice, and the symbol $\bar{1}$ indicates the presence of an inversion center as the only symmetry operation. Structures described by this space group are fully triclinic, with no rotational or mirror symmetry, and are often associated with strongly distorted high-pressure phases. The $\zeta\text{-Fe}_2\text{O}_3$ phase has iron in octahedra and prisms.

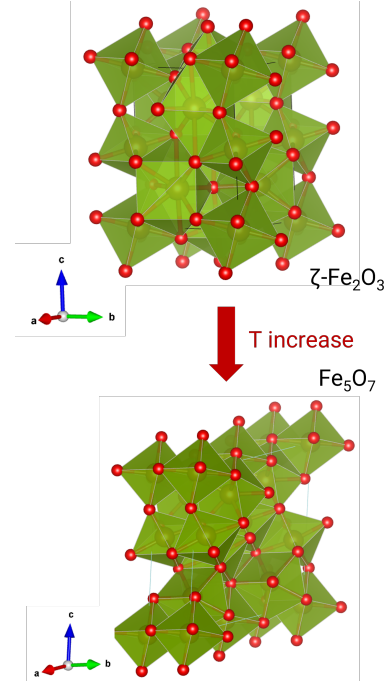
The post-perovskite-type phase of $\eta\text{-Fe}_2\text{O}_3$ is commonly described by the orthorhombic space group $Cmcm$. The letter C denotes base-centered lattice centering. The letters m indicate mirror planes, while c denotes a glide plane parallel to the c axis. This space group accommodates multiple crystallographically distinct iron sites (octahedra and prisms) with different coordination environments.

In some studies, high-pressure $\theta\text{-Fe}_2\text{O}_3$ phase, with iron in prisms, has been described using orthorhombic settings such as $Aba2$ or $Aea2$. In these symbols, the letter A denotes base-centered lattice centering, while the remaining letters indicate glide planes or mirror symmetries along specific crystallographic directions. Such alternative settings reflect different choices of unit-cell axes rather than fundamentally distinct symmetry classes.

The higher oxide Fe_5O_7 , formed upon heating Fe_2O_3 , crystallizes in the monoclinic system with space group $C2/m$ and is characterized by a framework of both octahedral and prismatic iron coordination polyhedra, as depicted in Fig. 5.3. The letter C denotes base-centered lattice centering, while the symbol 2 represents a twofold rotation axis.

The letter m indicates the presence of a mirror plane perpendicular to the rotation axis. This combination of symmetry elements reflects a lower symmetry compared to the parent Fe_2O_3 phases and accommodates multiple distinct iron sites (octahedra and prisms).

The higher oxide $\text{Fe}_{25}\text{O}_{32}$, formed under high-temperature conditions, crystallizes in the hexagonal system with space group $P\bar{6}2m$. The letter P denotes a primitive lattice, while the symbol $\bar{6}$ represents a sixfold rotoinversion axis. The number 2 indicates the presence of twofold rotation axes perpendicular to this axis, and m denotes mirror planes. This relatively high-symmetry space group accommodates a complex arrangement of iron sites with mixed coordination environments with octahedra and prisms.



5.3 Temperature determination

In order to achieve HT along with HP and perform *in situ* measurements, a portable laser-heating system [141] was set up at beamline P01 (see in Chapter 4.4 for detailed information). This chapter describes how temperature measurements were performed and subsequently the temperature was determined.

As previously described in Chapter 4.4 temperature measurements were performed by collecting the thermal emission of the glowing sample (black-body-radiation) and fitting the spectra with a Planck fit. Prior to the heating experiments, the spectrometer response was calibrated using a tungsten filament lamp of known temperature, which had been previously calibrated against a certified radiance standard (Gooch & Housego PLC), ensuring traceable spectral intensity. By recording the lamp spectrum through the same optical path as used during the experiment, the wavelength-dependent instrumental response function was determined. This calibration enabled accurate temperature determination of the laser-heated samples via Planck fitting of the measured thermal emission spectra.

The spectrometer entrance is equipped with a mirror containing two holes, enabling simultaneous observation of the sample and independent upstream/downstream temperature measurements. Spectra were acquired about every 4 s in a wavelength range between 581 and 832 nm. Laser power and therefore sample temperature were adjusted during the measurements. Uncertainties arise from spectrometer calibration, chromatic aberration of the optics, as well as axial and lateral temperature gradients within the sample. An in depth overview of laser-heating techniques is provided by Anzellini et al. [169].

The program T-Rax [170] is used for fitting and therefore temperature calculation during the experiment using the above-mentioned calibration. An example image of a temperature fit can be seen in Fig. 5.4.

Figure 5.3: Crystal structure of $\zeta\text{-Fe}_2\text{O}_3$ phase to Fe_5O_7 at HT based on Bykova et al. [11].

To reliably assign temperatures to the XES measurements, a dedicated post-experimental temperature evaluation was performed and is described hereinafter.

All temperature scans recorded during the experiment were compiled in a single overview file, which contains the corresponding scan numbers, laser powers, and experimental conditions. From this dataset, only scans acquired without X-ray illumination were manually selected for temperature calibration in order to avoid any influence of beam-induced effects on the thermal emission spectra. These scans were evaluated using a Python-based analysis routine that reproduces the T-Rax workflow, including spectral response correction using a calibrated tungsten lamp and fitting of the corrected spectra with a Planck function.

Temperature measurements were performed on the downstream side. Individual frames were filtered based on the uncertainty of the Planck fit, retaining only spectra with sufficient data quality. For each laser-heating interval (corresponding to a defined scan range at constant laser power), the accepted temperatures were averaged, and the standard deviation was calculated. When multiple consecutive heating scans were performed at the same laser power, the corresponding scan ranges were combined and an additional averaging step was applied to obtain a representative temperature for that power level. In the following these calculated temperatures were used, and a collective error was estimated to 200 K.

The final temperatures were assigned to the XES measurements by correlating each XES acquisition period with the corresponding laser-heating scan block and its associated laser power setting. This assignment was based on the chronological sequence of the scans and the documented scan ranges. By linking each XES dataset to the averaged temperature derived from its respective heating interval, a consistent temperature scale was established across all pressures and runs. Consequently, the XES spectra are analyzed as a function of calculated temperature rather than nominal laser power. These calculated temperatures are used throughout the following chapters when discussing temperature-dependent variations in the XES data.

5.4 Data processing

The XES and RXES datasets recorded at beamline P01 consist of detector images based on a pixel scale ($172 \times 172 \mu\text{m}^2$) that require several processing steps before quantitative comparison is possible. In particular, background subtraction and energy calibration is needed. The goal of the procedure described here, is to obtain energy-calibrated and normalized XES spectra and RXES maps that can be compared between measurements carried out at different pressures and temperatures. The following subsections describe the individual steps of the workflow, from data extraction and to energy calibration and

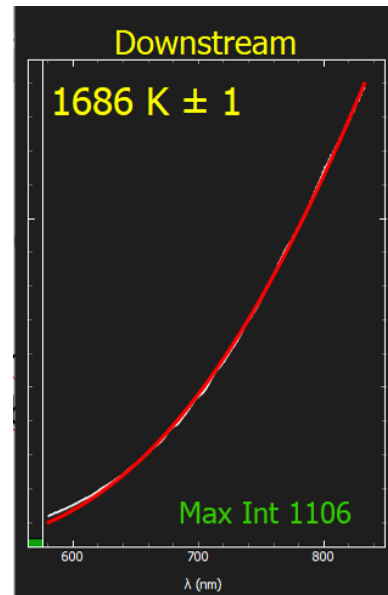


Figure 5.4: Screenshot from the T-Rax program displaying a scan during heating with the Planck fit in red for downstream and the calculated temperature.

final normalization. In addition, the processing of the XRD mapping data acquired at beamline P02.2 is described, including the normalization procedure applied to reflect relative spatial phase variations.

5.4.1 X-ray emission spectroscopy

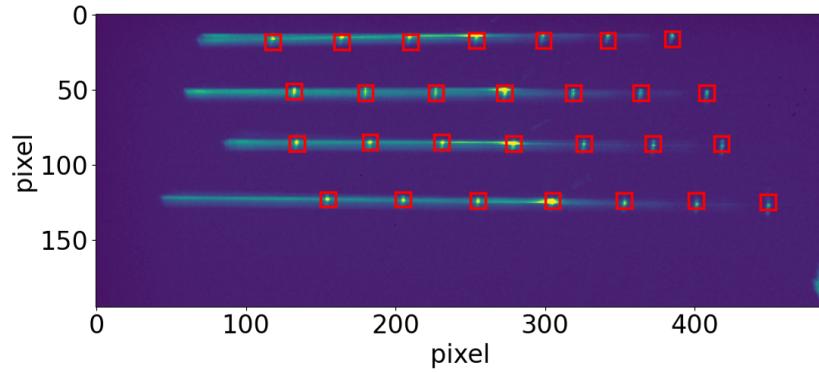


Figure 5.5: Detector image of the elastic scans including ROIs around the elastic scattering signal from the diamond at different incident energies varying between 10500 and 10680 eV.

The emission spectrum is wavelength-dispersed by the analyzer crystals and imaged onto the two-dimensional detector, with energy dispersion occurring along the vertical detector axis, while the signals from the individual analyzer crystals are spatially separated along the horizontal axis. For the energy calibration of the XES data, elastic scattering from the downstream diamond anvils is measured and used as an internal reference. This contribution provides well-defined energy markers on the detector plane.

For the calibration procedure, the incident energy is varied between 10500 and 10680 eV in several, here six, equidistant steps, with an acquisition time of 10 s per energy point. The Si(660) reflections of the analyzer crystals are used to measure elastic lines in contrast to the Si(440) reflections, which are used for emission measurements, such that the Bragg condition is fulfilled for different energies at slightly different angles. The scaling factor of 1.5 between the energy scans probed by the Si(660) and Si(440) reflections arises from the ratio of their lattice-plane spacings. For a cubic crystal such as silicon, the interplanar spacing is given by $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$, where a is the lattice parameter and (hkl) are the Miller indices.

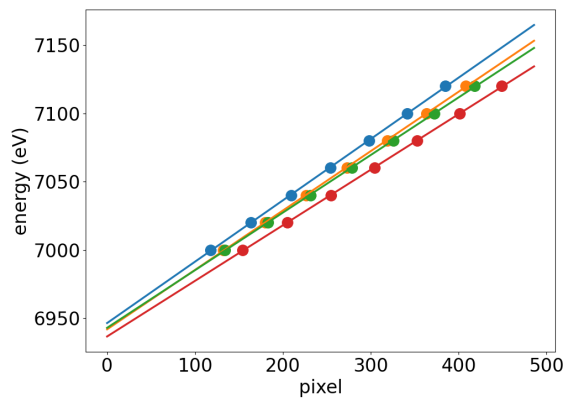


Figure 5.6: Peak positions for each crystal extracted via Gaussian fit containing energy information used for the energy calibration on the entire detector plane.

For the Si(440) reflection, inserting $h = 4$, $k = 4$, and $l = 0$ yields $d_{440} = \frac{a}{\sqrt{4^2+4^2+0^2}} = \frac{a}{\sqrt{32}}$. For the Si(660) reflection, inserting $h = 6$, $k = 6$, and $l = 0$ gives $d_{660} = \frac{a}{\sqrt{6^2+6^2+0^2}} = \frac{a}{\sqrt{72}}$.

The ratio of the lattice spacings is therefore $\frac{d_{440}}{d_{660}} = \frac{a/\sqrt{32}}{a/\sqrt{72}} = \sqrt{\frac{72}{32}} = 1.5$. Since, according to Bragg's law, the photon energy at fixed Bragg angle scales as $E \propto 1/d$, the Si(660) reflection corresponds to an energy that is 1.5 times higher than that of the Si(440) reflection at identical Bragg angles.

As a result, pronounced intensity maxima corresponding to elastically scattered photons appear on the detector, forming so-called elastic lines along the dispersive direction of the von Hámos spectrometer for each analyzer crystal. Since the setup is very sensitive to changes in geometry, it has to be repeated either before or after each change of the sample or after sample movement. A summed detector image over all incident energies and all four analyzer crystals is shown in Fig. 5.5, together with the selected regions of interest (ROIs) around the elastic scattering signals.

For each elastic line, a square ROI of typically 5×5 pixels is defined around the signal maximum. Within this region, the detector counts are integrated along the non-dispersive direction. A Gaussian function is then fitted to the resulting intensity profile in order to determine the peak position for each analyzer crystal and each incident energy. These peak positions correspond directly to the known incident energies and thus establish discrete energy-pixel reference points on the detector.

The extracted peak positions are plotted as a function of pixel coordinate for each analyzer crystal and fitted with a linear function, as illustrated in Fig. 5.6.

Following energy calibration, detector images from emission measurements acquired at a fixed incident energy, here 10400 eV via Si(440) reflection, are processed in an analogous manner. ROIs are defined for each analyzer crystal, and the detector counts are integrated in a range of 10 pixels along the non-dispersive direction to obtain individual emission spectra (cf. Fig. 5.7). To account for background contributions, the ROIs are shifted by 5 pixels above and below the signal region on the non-dispersion axis to estimate the background, which is subsequently smoothed, scaled, and subtracted from the emission signal. The final XES spectrum is obtained by summing the background-corrected spectra from all analyzer crystals after a check for consistency and normalized in area between 7020 and 7120 eV.

Integral of absolute difference for spin-state analysis

As an essential part of the XES data analysis, the integral of absolute difference (IAD) method [27] is employed to quantify changes in the electronic spin-state of iron. This

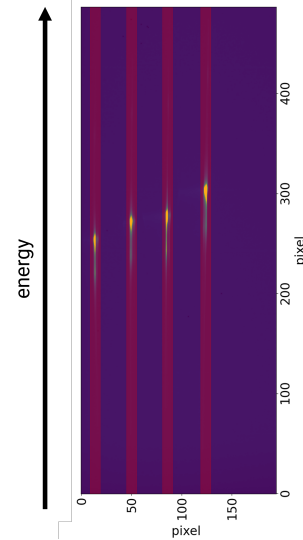


Figure 5.7: Detector image of emission measured at 10400 eV incident energy including ROIs around the signal. The portrait format matches the actual detector position during measurement with higher energies at higher pixels.

approach is based on a comparison of $\text{K}\beta$ emission spectra and provides a robust, model-independent measure of relative spin-state variations, if spectra are measured with high statistical accuracy.

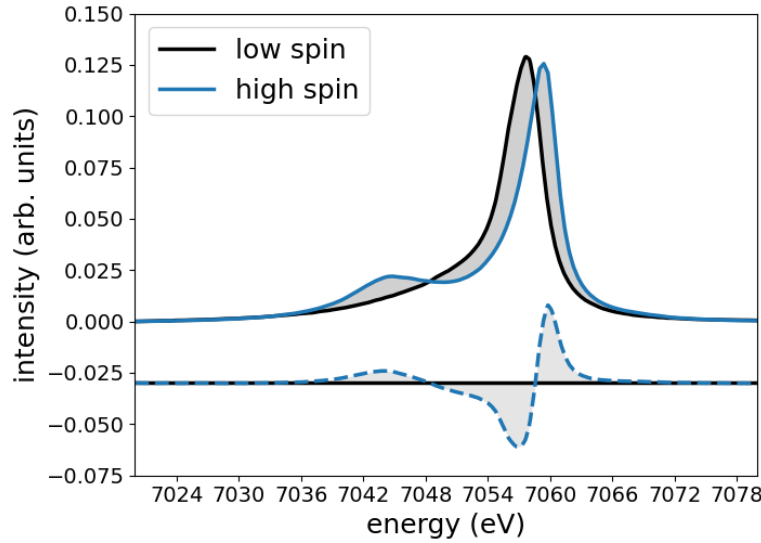


Figure 5.8: $\text{K}\beta$ XES spectra of iron in an HS (blue) and LS (black) state with their difference shifted in intensity (dashed line). The in gray colored area marks the difference used for integration.

Prior to the IAD calculation, all emission spectra are aligned to a common energy reference by shifting their center of mass (CMS) to the same emission energy. This step ensures that differences between spectra arise from changes in spectral shape rather than from residual energy misalignment. In this work, the CMS is shifted to a fixed reference energy (7055 eV) [28] close to its original position, allowing for consistent comparison between spectra.

The IAD value is obtained by subtracting a reference spectrum with a known spin-state from the spectrum under investigation and integrating the absolute value of the resulting difference curve over the emission energy range between 7035 and 7070 eV (cf. Fig. 5.8). The integrated area corresponds to the IAD value and reflects the magnitude of the spectral changes induced by variations in the spin-state and to a lesser extent variations in the local geometry. Using reference spectra representative of different spin configurations, the IAD values can be related to relative changes in the average spin-state of iron. The reference LS state spectrum used in the following analysis is FeCO_3 at 80 GPa with a spin of zero.

Generally, the IAD method provides relatively robust results for spectra with moderate noise

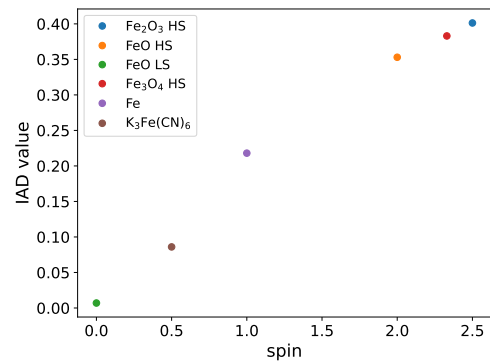


Figure 5.9: IAD values with assigned spin-states extracted from Lafuerza et al. [28] and adjusted to fit the IAD values in the following analysis. The FeO in HS state is unpublished.

levels and is therefore well suited for the analysis of experimental XES data acquired under extreme pressure and temperature conditions. However, a source of uncertainty in the IAD analysis arises from inaccuracies in the CMS alignment and from the noise level itself. Small errors in the energy shift can lead to systematic changes in the IAD value, especially for spectra close to the spin-state of the reference spectra. For spectra with reasonable signal quality, the uncertainty in the CMS alignment is typically limited to a fraction of an eV, resulting in an estimated error on the order of ten percent of a complete HS to LS transition. This uncertainty is taken into account when interpreting the IAD-derived spin-state trends [115].

Typical IAD values associated with different spin states are shown in Figure 5.9, based on data from [28]. To ensure consistency with the present analysis, these reference values were systematically shifted. Specifically, the high-spin (HS) IAD value for Fe_2O_3 at 13 GPa determined in this study (0.40127 for $S=2.5$) deviates from the corresponding value reported by Lafuerza et al. (0.467) by 0.066. Therefore, all IAD values from [28] were uniformly reduced by this offset (0.066) to align them with the HS reference value obtained here.

5.4.2 Valence-to-core emission

In the Fe $K\beta$ emission region, the weak vtc features are observable on the high-energy tail of the intense $K\beta_{1,3}$ main line. In order to reliably analyze the vtc spectral shape and relative intensity, the slowly varying contribution of the $K\beta_{1,3}$ tail must be modelled and removed. For this purpose, a dedicated background subtraction routine was implemented.

The function operates on normalized spectra and performs an empirical modelling of the $K\beta_{1,3}$ high-energy tail within the energy range 7065-7120 eV. For each spectrum, the full energy axis E and normalized intensity $I(E)$ are extracted. Rather than fitting the entire tail region, the fit is constrained to selected support windows that show hardly any contribution of distinct vtc features. This approach ensures that the model reproduces the smooth tail of the main line without adapting to fine spectral structures that belong to the vtc signal.

The tail is described by a Pseudo-Voigt profile combined with a background,

$$I_{\text{model}}(E) = \text{PV}(E; \sigma, \mu, A, \alpha) + b, \quad (5.1)$$

where σ denotes the width parameter, μ the peak position, A the amplitude, and α the mixing parameter between Lorentzian and Gaussian contributions and b for the constant background. The initial peak position is placed close to the $K\beta_{1,3}$ maximum (approximately 7056 eV). Fig. 5.10 shows the original data including the fit and the result. Due to the energy shift of features depending on pressure and temperature, the supporting windows haven been correspondently adapted. By restricting the fit to carefully selected support windows, the procedure provides a reproducible and robust separation of the weak vtc signal from the dominant main-line background.

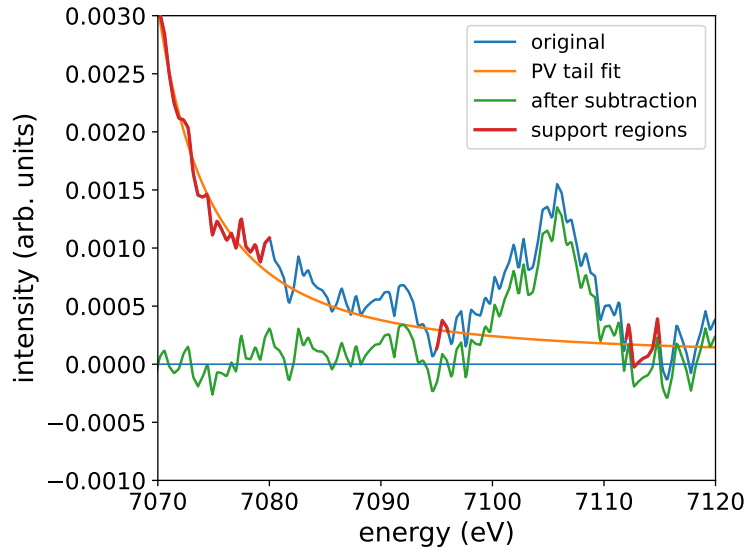


Figure 5.10: Vtc spectrum of Fe_2O_3 at 38 GPa (blue) including the Pseudo-Voigt fit (orange) and its supporting regions (red) as well as the subtracted data afterwards (green).

5.4.3 Resonant X-ray emission spectroscopy

For the RXES measurements at incident energies between 7090 and 7300 eV via $\text{K}\alpha$ emission, Si(111) analyzer crystals and their Si(333) reflection were used for detection of the emission energy around 6400 eV.

RXES datasets are evaluated on the basis of two-dimensional intensity maps, in which the incident energy is scanned while the emitted signal is recorded dispersively on the detector. For further analysis, the measured images are converted into an RXES map on an energy-transfer grid, defined as

$$E_{trans} = E_{inci} - E_{em}, \quad (5.2)$$

with E_{trans} as the transfer energy, E_{inci} as the incident energy and E_{em} as the emitted energy. This representation allows direct comparison of spectral features as a function of incident energy and energy transfer. The emission energy axis is obtained from calibration scans measuring elastic scattering. Similar to the XES procedure described above, elastically scattered photons measured at several known incident energies (10630-10730 eV, Si(555) reflection, d-spacing factor 5/3) provide reference positions on the detector for each analyzer crystal. A pixel-to-energy relation is determined for each crystal and applied to the corresponding ROIs in the detector images.

In order to account for variations in incident intensity during the scan, the integrated spectra are normalized to the incident intensity I_0 recorded by a PIN diode. The resulting intensity is accumulated into a two-dimensional array to form the RXES map (cf. Fig. 5.11 top)). In practice, the signal ROI is shifted to the dispersive axis and the counts are integrated.

From the calibrated RXES map, spectra are analyzed in two complementary ways. CEE cuts, corresponding to HERFD-XANES (cf. Fig. 5.11 bottom left)), are obtained by

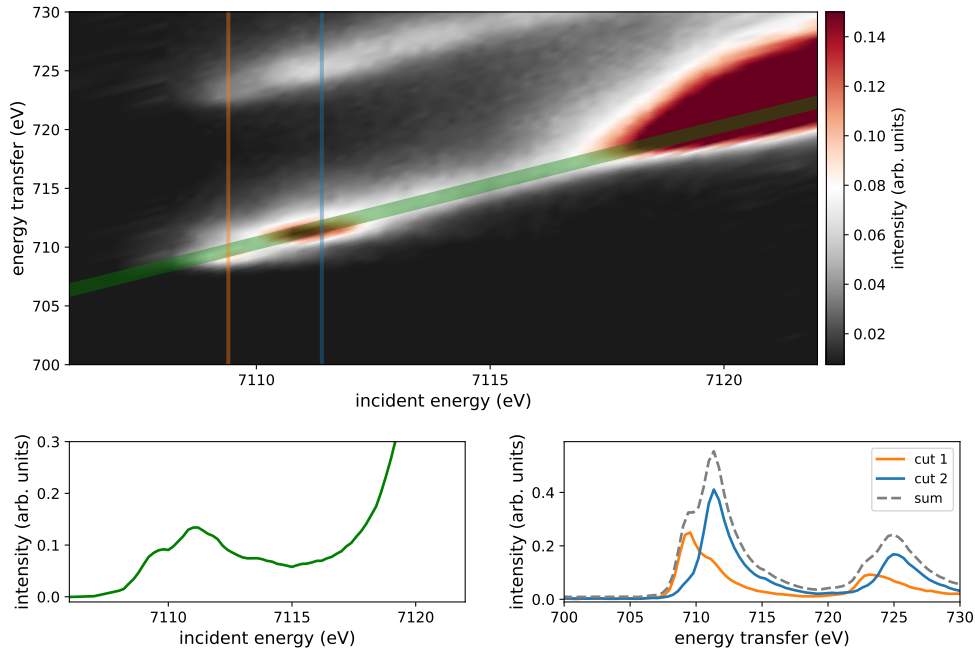


Figure 5.11: Top) RXES map with cuts for bottom left) CEE resulting in a HERFD-XANES spectrum and bottom right) CIE presenting L-edge like spectra. The gray dashed line is enveloping the two cuts for a summed spectrum. The colors of the spectra correspond with the colors of the cuts. In the subsequent analysis the area between 7109 and 7112 eV is integrated.

integrating the RXES intensity over a defined window in emission energy around the selected emission line. The chosen integration width represents a compromise between energy resolution and counting statistics and is implemented in the present work by summing several adjacent detector rows around the selected emission-energy index. CIE cuts are obtained by extracting emission spectra at fixed incident energy and represent L-edge like spectra (cf. Fig. 5.11 bottom right)). To improve the signal-to-noise ratio, neighboring incident-energy points can be integrated by summing adjacent columns of the RXES map.

5.4.4 X-ray diffraction

XRD data were acquired using a raster scan approach at a wavelength of 0.2906 nm, enabling spatially resolved phase analysis across the sample chamber. A step size of 2 μm and an exposure time of 4 s per scan point were employed. The dimensions of the scanned areas varied and amounted to 17×17 points for measurements at 38 and 80 GPa, corresponding to 289 diffraction images per sample, and 21×31 points for the experiment at 64 GPa, yielding a total of 651 images.

Instrument calibration was performed using a CeO_2 (cerium oxide) calibrant, which is certified as a standard reference material by the National Institute of Standards and Technology (NIST) [171]. The diffraction data were initially analyzed using the software Dioptas [172], where representative diffraction patterns were selected for phase identification. Based on the phase assignment, two-dimensional phase distribution

maps were subsequently generated using a custom Python script incorporating all available diffraction images per sample. This approach allows visualization of the spatial distribution and relative contributions of different phases within the sample region.

The diffraction patterns obtained from the sample typically exhibit pronounced diffraction spots rather than continuous Debye-Scherrer rings, indicating that diffraction arises from a limited number of crystallites satisfying the Bragg condition [65, 93]. This characteristic complicates phase identification. To improve phase assessment, the diffraction images were transformed into polar coordinates and visualized as so-called cake views, displaying intensity as a function of 2Θ and azimuthal angle. This representation preserves azimuthal information and facilitates comparison with reference diffraction patterns in Dioptas.

For the spatial phase maps, each raster point was subsequently azimuthally integrated over the full azimuthal range to obtain a one-dimensional diffraction pattern $I(2\Theta)$ using the calibrated detector geometry. A smooth background was estimated from the azimuthally integrated pattern by applying iterative Bruckner smoothing followed by fitting a high-order Chebyshev polynomial to the smoothed intensity baseline. Bruckner smoothing is an iterative baseline-estimation algorithm that progressively suppresses sharp Bragg peaks while preserving the slowly varying intensity contribution of the diffraction pattern. The resulting smoothed baseline was then approximated by a Chebyshev polynomial, whose orthogonal basis functions provide a numerically stable and flexible representation of the continuous background over the finite 2Θ interval. The fitted background function was subsequently subtracted prior to peak integration. Phase-specific intensity maps were then generated by integrating the background-subtracted intensity within narrow 2Θ windows around selected Bragg reflections of each candidate phase and summing the contributions of all selected reflections. The resulting map values corresponds to the sum of the integrated intensities of the selected Bragg reflections of that phase at each raster position.

To reduce biases arising from the arbitrary choice of reflections and from differences in intrinsic scattering strength between phases, an intensity normalization was applied using calculated powder patterns. For each phase, a calculated powder pattern (generated using Mercury [173], from .cif files provided by Bykova et al. [11]) was integrated over the full measured angular range (0° - 25° in 2Θ) to obtain the total calculated intensity $I_{\text{full}}^{\text{calc}}$. The experimental phase maps were then normalized by dividing the integrated peak intensities at each raster position by $I_{\text{full}}^{\text{calc}}$. This procedure accounts for differences in intrinsic scattering strength (at similar stoichiometries) between phases and ensures that the resulting maps reflect relative spatial variations in phase contributions rather than differences arising from the number or selection of Bragg reflections.

Since the scattering angle 2Θ depends on the experimental geometry and the incident X-ray energy, the diffraction data are expressed in terms of the absolute value of the scattering vector $|\vec{q}|$, which provides a setup-independent representation and facilitates comparison with results from the literature. The conversion from scattering angle to momentum transfer is given by Eq. 3.11, where the wavelength λ is related to the photon energy E via

$$\lambda(\text{\AA}) = \frac{12.3984}{E(\text{keV})}. \quad (5.3)$$

5.5 Experimental results

In the following, the experimental results obtained for Fe_2O_3 at beamline P01 are presented. The $\alpha\text{-Fe}_2\text{O}_3$ powder sample was purchased from Sigma-Aldrich (99.995% trace metal basis). The measurements were performed at pressures of 38, 64, and 80 GPa. The presentation begins with XES, which provides direct insight into the local electronic structure, the spin-state of iron. These results are complemented by XRD measurements, which allow the identification of pressure-induced structural phase transitions. Finally, RXES is used to verify and further constrain the electronic and structural interpretations derived from XES and XRD.

5.5.1 X-ray emission spectroscopy

In the following results from XES in the regions of the $\text{K}\beta_{1,3}$ emission as well as vtc region with $\text{K}\beta_{2,5}$ emission are presented. Spin-state analysis based on the spectral features and IAD values are provided based on $\text{K}\beta_{1,3}$ emission.

5.5.1.1 $\text{K}\beta_{1,3}$ emission – spin-state

XES spectra acquired for Fe_2O_3 at pressures of 38, 64 and 80 GPa before, during, and after laser heating are presented. In addition, the difference spectra with respect to a LS ($S=0$) reference spectrum of FeCO_3 measured at 80 GPa are displayed beneath the corresponding XES data. In the following, the evolution of the spectral shape and the associated changes in the electronic spin-state are described. A comparison between all measures spectra at room temperature are shown in the Appendix Fig. A.18.

38 GPa For the measurement at 38 GPa (cf. Fig. 5.12), the XES spectrum before heating shows HS state features with the shoulder of the $\text{K}\beta'$ at around 7045 eV. Especially the comparison to the LS reference highlights the HS state character of Fe_2O_3 at 38 GPa. Selected spectra during heating between 1975 and 2026 K do not show changes in line shape. Likewise, the spectrum measured after heating (quenched) exhibits comparable spectral characteristics. Within the experimental resolution, the spectra recorded before, during, and after heating are indistinguishable. This observation is corroborated by the corresponding difference spectra shown below. Whether laser heating induces a structural phase transition at this pressure is addressed by complementary XRD measurements.

To complement the qualitative inspection of the XES spectra, the IAD values were calculated for all measurements. The resulting IAD values for 38 GPa are shown in Fig. 5.12 in the inset. The IAD values determined during heating and after quenching overlap within the experimental uncertainty, while the value obtained before heating also lies within the same range. The uncertainty of the IAD values is estimated as 10% of the maximum IAD value observed within this pressure series, corresponding to ± 0.039 .

The individual IAD values obtained at 38 GPa are summarized in Tab. 5.2. During heating, the IAD values range between 0.371 and 0.391, yielding an average value of $\text{IAD}_{\text{heated}} = 0.379 \pm 0.008$. The spectra recorded before and after heating exhibit IAD values of 0.359 and 0.380, respectively. The deviations of these values from the mean

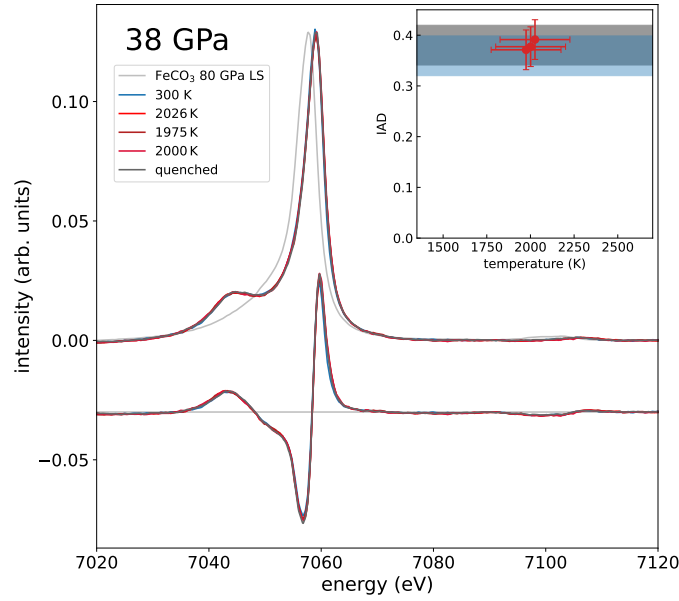


Figure 5.12: XES spectra before (blue) during (red hues, selected) and after (quenched, dark gray) heating at 38 GPa with the difference to LS spectrum FeCO_3 at 80 GPa (light gray) shifted in intensity. The inset are the IAD values depending on the temperature with error, before (blue) and after (dark grey) heating. The red points with their error present the IAD values during heating and their temperature.

heated IAD amount to 0.019 and 0.002, respectively, both of which are smaller than the estimated experimental uncertainty.

64 GPa When examining the XES spectra measured at 64 GPa in Fig. 5.13 and comparing the spectrum recorded before heating to the data at 38 GPa, a decrease of the $\text{K}\beta'$ shoulder and a shift of the main emission features towards lower energies are observed. These changes are consistent with a reduction of the average spin-state compared to the 38 GPa spectra to a mixed-spin-state, possibly as a result of structural changes.

A comparison with the LS reference spectrum of FeCO_3 shows that the Fe_2O_3 spectrum at 64 GPa does not correspond to a fully low-spin configuration, indicating a mixed spin-state. During laser heating, the intensity of the $\text{K}\beta'$ feature increases slightly, accompanied by a shift of the main peak $\text{K}\beta_{1,3}$ towards higher energies. The corresponding difference spectra displayed below the XES data illustrate these changes, which is also observed for the spectrum recorded after quenching.

The corresponding IAD values for the measurements at 64 GPa are summarized in Tab. 5.3. The IAD value obtained before heating amounts to 0.120, whereas the spectra recorded during heating yield values between 0.160 and 0.196, resulting in a mean heated value of $\text{IAD}_{\text{heated}} = 0.176 \pm 0.018$. The deviation of the pre-heating IAD value from the heated mean is 0.056, which exceeds the estimated experimental uncertainty of ± 0.039 . After quenching, the IAD value of 0.171 deviates from the heated mean by 0.005 and thus remains within the experimental uncertainty. Fig. 5.13 in the inset visualizes the

Table 5.2: IAD values derived from Fe_2O_3 XES spectra at 38 GPa before, during, and after laser heating. The uncertainty is estimated as 10% of the maximum IAD value at this pressure.

	value
IAD before heating	0.359
IAD during heating (individual values)	
T=1877 K	0.391
T=1616 K	0.371
T=2026 K	0.377
T=1975 K	0.373
T=1823 K	0.374
T=2001 K	0.384
mean IAD during heating	0.379
standard deviation (heated)	0.008
IAD after heating	0.380
absolute deviation before heating	0.019
absolute deviation after heating	0.002
estimated uncertainty (10%)	± 0.039

increase in IAD values during heating relative to the pre-heating state and its persistence after quenching.

80 GPa At the highest pressure of 80 GPa, the XES spectrum measured before laser heating is close to the LS reference spectrum of FeCO_3 (cf. Fig 5.14), consistent with a predominantly LS character. During laser heating, the XES spectra exhibit the emergence of a $\text{K}\beta'$ pre-peak accompanied by a shift of the main emission peak towards higher energies. These spectral changes are clearly visible in the corresponding difference spectra shown below the XES data. The spectrum recorded after quenching displays intermediate spectral characteristics between the pre-heating and high-temperature states, which are likewise highlighted in the difference spectra.

The IAD values derived from the XES spectra at 80 GPa are summarized in Tab. 5.4 (right). Prior to heating, the IAD value amounts to 0.078. Since the reference spectrum of FeCO_3 at 80 GPa is in LS state with $S=0$, the expected difference between these IAD values is about 0.05 and with the measured IAD value of 0.078 this would be within the error and account for a full LS state of $S=0.5$. During laser heating, the IAD values range between 0.293 and 0.308, yielding a mean value of $\text{IAD}_{\text{heated}} = 0.301 \pm 0.008$. The deviation of the pre-heating IAD value from the heated mean is 0.223, which is significantly larger than the estimated experimental uncertainty of ± 0.039 . After quenching, the IAD value decreases to 0.209, corresponding to a deviation of 0.093 from the heated mean, which likewise exceeds the experimental uncertainty.

Fig. 5.14 (inset) illustrates the increase of the IAD values during heating compared to the pre-heating state and the partial relaxation observed after quenching.

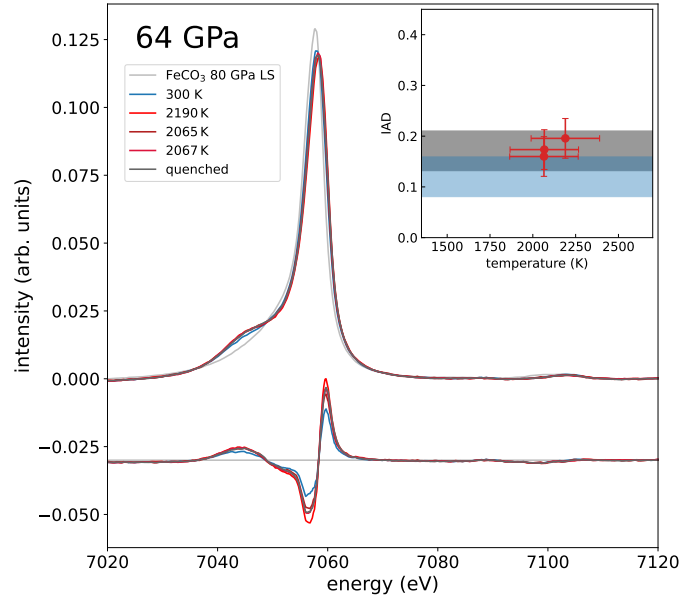


Figure 5.13: XES spectra before (blue) during (red hues, selected) and after (quenched, dark gray) heating at 64 GPa with the difference to LS spectrum FeCO_3 at 80 GPa (light gray) shifted in intensity. The inset are the IAD values depending on the temperature with error, before (blue) and after (dark grey) heating. The red points with their error present the IAD values during heating and their temperature.

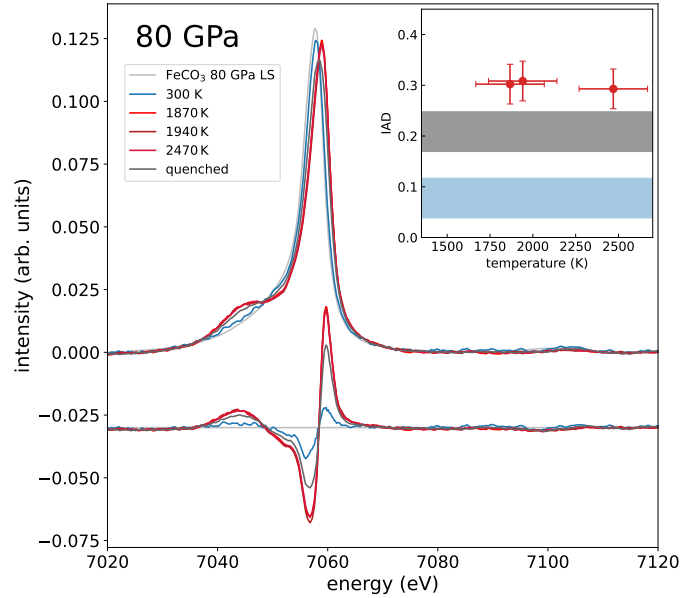


Figure 5.14: XES spectra before (blue) during (red hues, selected) and after (quenched, dark gray) heating at 80 GPa with the difference to LS spectrum FeCO_3 at 80 GPa (light gray) shifted in intensity. The inset are the IAD values depending on the temperature with error, before (blue) and after (dark grey) heating. The red points with their error present the IAD values during heating and their temperature.

Table 5.3: IAD values derived from Fe_2O_3 XES spectra at 64 GPa before, during, and after laser heating. The uncertainty is estimated as 10% of the maximum IAD value from the 38 GPa pressure point.

	value
IAD before heating	0.120
IAD during heating (individual values)	
T=2190 K	0.196
T=2065 K	0.160
T=2067 K	0.174
mean IAD during heating	0.176
standard deviation (heated)	0.018
IAD after heating	0.171
absolute deviation before heating	0.056
absolute deviation after heating	0.005
estimated uncertainty	± 0.039

Table 5.4: IAD values derived from Fe_2O_3 XES spectra at 80 GPa before, during, and after laser heating. The uncertainty is estimated as 10% of the maximum IAD value determined at 38 GPa.

	value
IAD before heating	0.078
IAD during heating (individual values)	
T=1867 K	0.302
T=1941 K	0.308
T=2470 K	0.293
mean IAD during heating	0.301
standard deviation (heated)	0.008
IAD after heating	0.209
absolute deviation before heating	0.223
absolute deviation after heating	0.093
estimated uncertainty	± 0.039

5.5.1.2 $\text{K}\beta_{2,5}$ valence-to-core emission

The position of the $\text{K}\beta_{2,5}$ peak was determined by fitting a Gaussian function to the background-subtracted vtc spectra using Python. Fits were performed in a restricted energy window around the peak maximum (7102-7109 eV), and the fitted peak center (μ) was used to calculate energy shifts relative to the room-temperature spectrum. The table containing all $\text{K}\beta_{2,5}$ peak positions from the Gaussian fit are listed in the Appendix Tab. A.7. A Savitzky-Golay filter [174] was applied to the spectra to reduce noise for visualization purposes. The filter is based on a polynomial fit within a sliding window, which minimizes distortion of peak shapes and positions compared to conventional averaging methods.

The vtc spectra measured at **38 GPa** (cf. 5.15) show a subtle shift of the $\text{K}\beta_{2,5}$ peak from around 7105.8 eV towards higher energies of 1 eV at the highest temperature. This shift is reversible upon temperature quenching. The $\text{K}\beta''$ pre-peak at around 7090 eV is

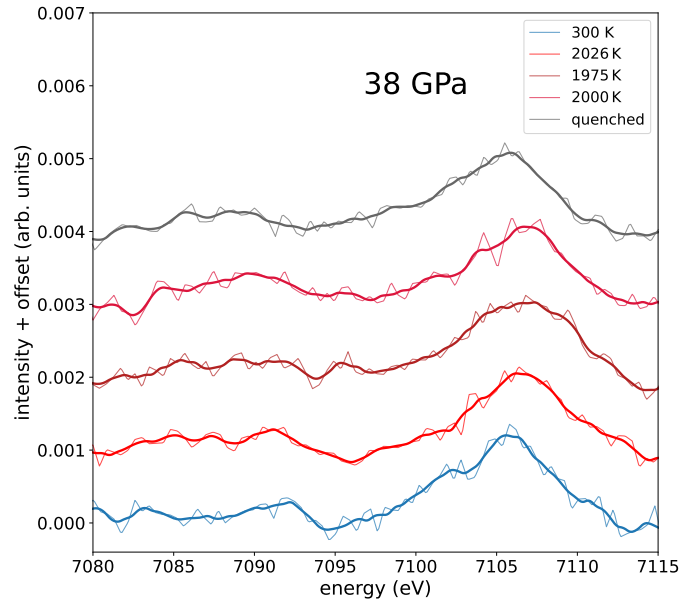


Figure 5.15: Vtc spectra at 38 GPa shifted in intensity before heating (blue), during heating (red hues) and temperature-quenched (grey) less saturated with Savitzky-Golay filtered spectra on top for better visualization.

only weakly developed in these spectra, and the limited signal-to-noise ratio prevents a more detailed evaluation.

At **64 GPa** (cf. 5.16) the $\text{K}\beta_{2,5}$ peak position is systematically shifted towards lower energies (to $\approx 7103\text{ eV}$) by approximately 2-3 eV compared to 38 GPa. The main peak is slightly decreased in intensity with higher temperatures and partially relaxes after quenching to intensities in between before and during heating. A shift in energies is not clearly observable between all the collected spectra. In contrast to 38 GPa, the $\text{K}\beta''$ here is more pronounced and exhibits a similar spectral shape before, during, and after heating.

A comparison between the spectra recorded at **80 GPa** (Fig. 5.17) to 38 and 64 GPa is challenging, due to the data quality. Alas, a decrease in peak intensity during heating, which persists after quenching, is observed. However, at 80 GPa the peak position during and after heating is marginally shifted ($\approx 0.8\text{ eV}$) towards higher energies, a behavior not observed at 64 GPa. The $\text{K}\beta''$ pre-peak remains weak and is comparable to that observed at 38 GPa.

Fig. 5.18 shows the comparison between the pressures before, during, and after heating. Unfortunately, the data quality at 80 GPa, particularly before heating, is insufficient for a reliable comparison. The $\text{K}\beta''$ cross-over peak is highly sensitive to the metal-ligand distance [64]. The increased $\text{K}\beta''$ intensity observed at 80 GPa therefore indicates a shorter Fe-O bond distance and stronger metal-ligand interaction compared to 38 and 64 GPa. This behavior is particularly pronounced during heating. Fig. 5.18 also highlights differences in the energy position of the $\text{K}\beta_{2,5}$ feature. The spectra at 64 and 80 GPa exhibit similar peak positions, whereas the 38 GPa spectra are consistently shifted towards higher energies. The shift to lower energies with increasing pressure is consistent with Spiekermann et al. [175]. Since the $\text{K}\beta_{2,5}$ emission arises from valence-to-core

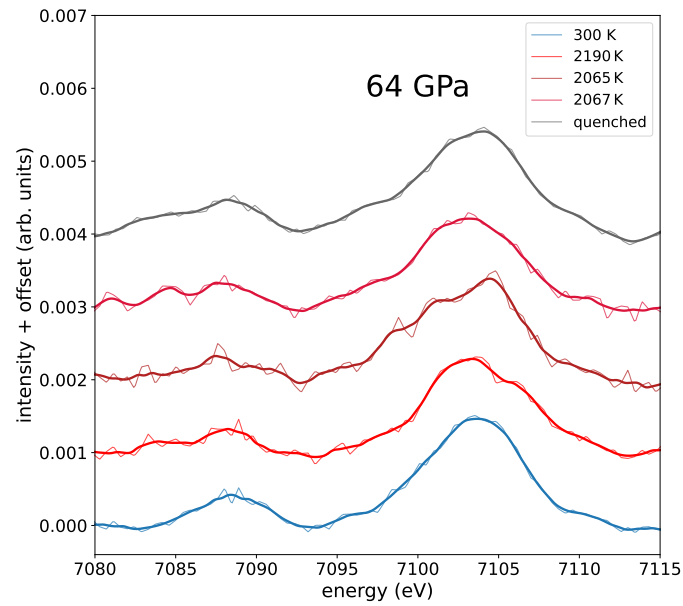


Figure 5.16: Vtc spectra at 64 GPa shifted in intensity before heating (blue), during heating (red hues) and temperature-quenched (grey) with Savitzky-Golay filtered spectra layered on top.

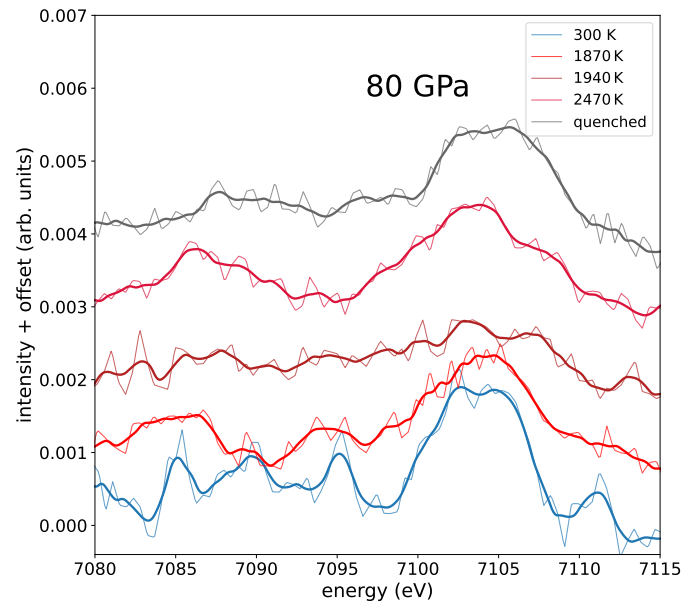


Figure 5.17: Vtc spectra at 80 GPa shifted in intensity before heating (blue), during heating (red hues) and temperature-quenched (grey) with Savitzky-Golay filtered spectra layered on top. The data quality before heating and at 1940 K is insufficient for a reliable comparison.

transitions involving ligand- and metal-derived occupied orbitals, its energy position reflects changes in the occupied valence electronic structure and metal-ligand interaction. In contrast to the $\text{K}\beta''$ cross-over peak, its interpretation cannot be attributed to a single structural parameter, but instead requires consideration of orbital composition, symmetry, and hybridization [64].

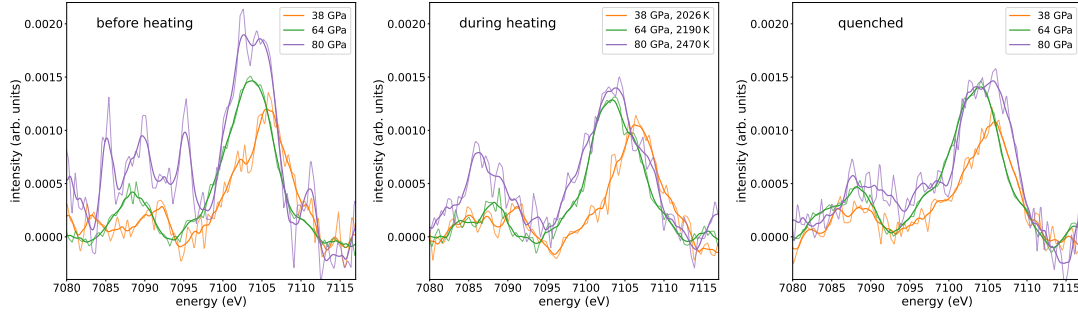


Figure 5.18: Vtc spectra at 38, 64, and 80 GPa comparing **left)** before heating, **middle)** during heating at their respective highest temperature, and **right)** after quenching. Smoothed spectra by Savitzky-Golay filter are shown as solid lines, while raw spectra are displayed with reduced opacity.

In summary, the XES results, comprising both the $\text{K}\beta_{1,3}$ spin-state analysis and the $\text{K}\beta_{2,5}$ valence-to-core spectra, reveal distinct behavior at the three investigated pressure points during and after laser heating. To assess whether structural phase transformations are responsible for these differences, complementary XRD measurements were conducted and are presented in the following section.

5.5.2 X-ray diffraction

Phase analysis after pressurization and laser heating was carried out via XRD at beamline P02.2 at PETRA III, DESY. This beamline is optimized for XRD experiments under extreme pressure conditions using DACs [176]. The experiments were performed at an incident X-ray energy of 42.7 keV. Phase assignment was carried out with particular care and precision. Especially for closely spaced diffraction spots, not only the peak position but also the peak shape and overall appearance was taken into account throughout to enable reliable phase differentiation. Consequently, only unambiguously assigned peaks are shown in the cake views presented later and in the appendix. For the XRD maps, only peaks sufficiently separated from reflections belonging to other phases were taken into account.

The cake view obtained at **38 GPa** (Fig. 5.19) reveals the coexistence of multiple phases after laser heating. In addition to diffraction peaks from the rhenium gasket and argon, reflections corresponding to the initial $\alpha\text{-Fe}_2\text{O}_3$ phase are observed along with additional peaks that can be assigned to the HT $\iota\text{-Fe}_2\text{O}_3$ phase. Not all observed diffraction features can be unambiguously assigned due to peak overlap and the presence of strong speckling. To avoid speculative phase assignments, only reflections that could be clearly attributed were considered in the analysis.

The corresponding two-dimensional phase distribution maps for Fe_2O_3 at 38 GPa are shown in Fig. 5.20. The $\alpha\text{-Fe}_2\text{O}_3$ phase (Fig. 5.20 left) is distributed relatively

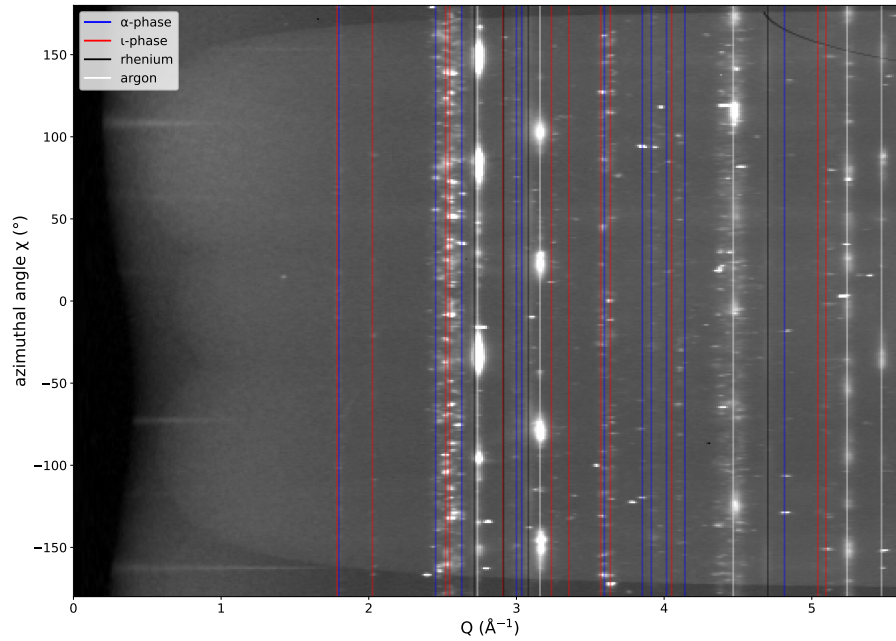


Figure 5.19: XRD cake view of image 162 at 38 GPa was exemplary used for phase identification. It shows unambiguously allocated phases in different colors. Next to the initial α - Fe_2O_3 phase (blue) the HT phase ι - Fe_2O_3 (red) is prevalent. For completeness argon (white) and rhenium (black) are also marked.

homogeneously across the sample chamber. Its persistent presence throughout the mapped area indicates that the transformation to the HP phase was incomplete under these conditions. In contrast, the ι - Fe_2O_3 phase (Fig. 5.20 right) is spatially localized and concentrated in a confined region.

The laser-heated region was operationally defined as the area exhibiting a significantly enhanced fraction of the HT phase. To aid spatial interpretation, the sample outline was extracted from a photograph of the sample in the beampath by grayscale thresholding and contour detection and subsequently overlaid onto the XRD maps after manual scaling and alignment. This overlay provides a visual reference for spatial correlation.

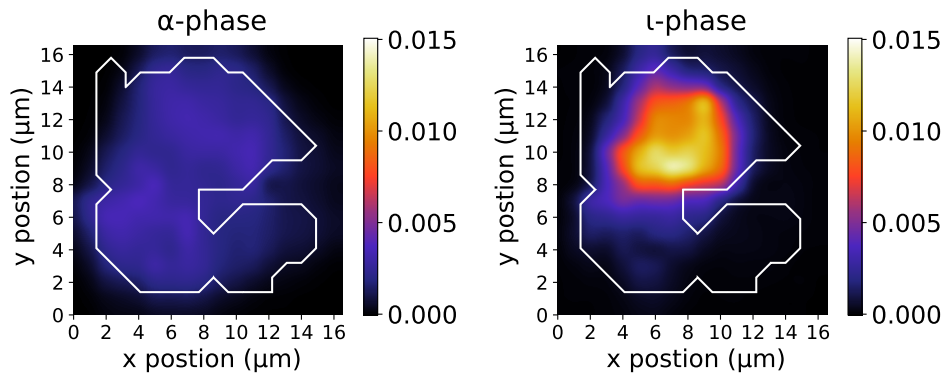


Figure 5.20: XRD 2D-map of 38 GPa with the white sample outline. **Left)** α - Fe_2O_3 phase and **right)** ι - Fe_2O_3 .

To complement the qualitative interpretation of the XRD maps, selected points were evaluated quantitatively by calculating the relative contributions of the identified phases. Three representative positions were chosen to capture the spatial variation across the sample. It is important to note that these values do not represent absolute phase abundances. Instead, they reflect the relative contributions of the selected diffraction peaks assigned to each phase and may be influenced by the chosen peak set as well as the normalization to calculated reference intensities.

For the dataset at 38 GPa, the central heated region at $(x, y) = (7, 9)$ is dominated by the $\iota\text{-Fe}_2\text{O}_3$ phase with 77.9%, while the $\alpha\text{-Fe}_2\text{O}_3$ phase contributes 22.1%. At the edge of the heated region (7, 12), a more mixed signal is observed, with 63.9% $\iota\text{-Fe}_2\text{O}_3$ phase and 36.1% $\alpha\text{-Fe}_2\text{O}_3$ phase. In contrast, a seemingly non-heated region (7, 3) is clearly dominated by the $\alpha\text{-Fe}_2\text{O}_3$ phase (88.6%), with only a minor $\iota\text{-Fe}_2\text{O}_3$ phase contribution of 11.4%.

Inspection of the XRD cake view at **64 GPa** for Fe_2O_3 (cf. Fig. 5.21) reveals a more complex phase assemblage compared to the experiment at 38 GPa. In addition to the initial $\zeta\text{-Fe}_2\text{O}_3$ phase, reflections attributable to the HT phase $\eta\text{-Fe}_2\text{O}_3$ are observed. Furthermore, diffraction features corresponding to the higher iron oxides Fe_3O_4 , Fe_4O_5 , and Fe_5O_7 can be identified.

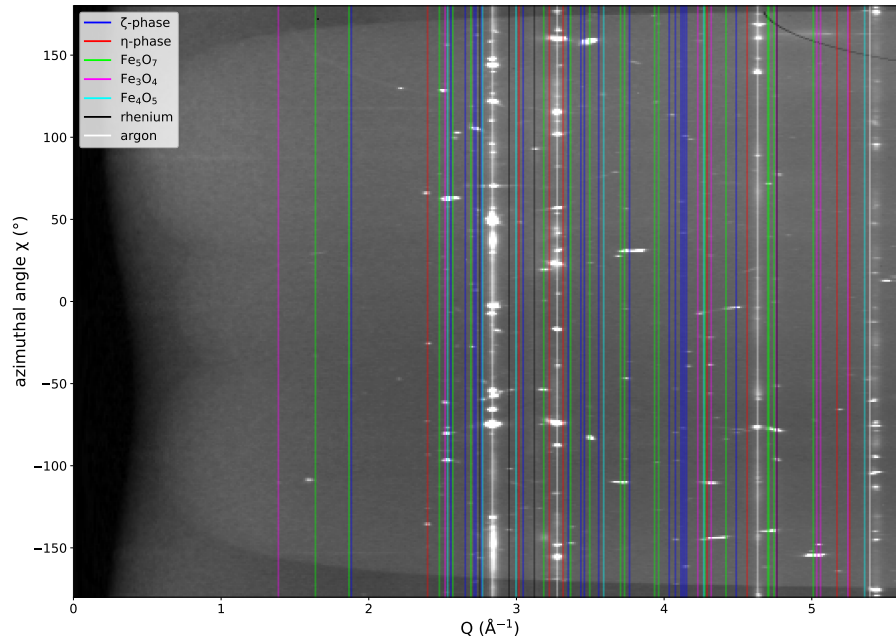


Figure 5.21: XRD cake view of image 160 at 64 GPa used for phase identification. The initial $\zeta\text{-Fe}_2\text{O}_3$ phase (blue), the HT phase $\eta\text{-Fe}_2\text{O}_3$ (red) are indicated, together with reflections from higher oxides Fe_3O_4 (pink), Fe_4O_5 (light blue) and Fe_5O_7 (green). Contributions from argon (white) and the rhenium gasket (black) are marked for completeness.

The associated spatial phase distribution maps are shown in Fig. 5.22. The maps are cropped, as the original raster scan encompassed additional samples loaded within the same sample chamber. The spatial distribution indicates negligible contributions from the initial $\zeta\text{-Fe}_2\text{O}_3$ phase, as well as small amounts of $\eta\text{-Fe}_2\text{O}_3$, Fe_4O_5 , and Fe_3O_4 . In

contrast, Fe_5O_7 exhibits a pronounced and spatially confined intensity maximum at the center of the mapped area, which coincides with the laser-heated region.

A similar quantitative evaluation as for 38 GPa was performed for the dataset at 64 GPa using three representative positions to characterize the spatial distribution of phases. As before, the reported values represent relative contributions of selected diffraction peaks and do not correspond to absolute phase abundances.

In the central heated region at $(x, y) = (25, 5)$, the signal is strongly dominated by Fe_5O_7 (79.6%), with a notable contribution from Fe_3O_4 (14.7%), while the $\eta\text{-Fe}_2\text{O}_3$ phase (5.3%) and $\zeta\text{-Fe}_2\text{O}_3$ phase (0.2%) are only minor components. At a position associated with increased $\zeta\text{-Fe}_2\text{O}_3$ phase contribution (25, 7), Fe_5O_7 remains the dominant phase (72.8%), accompanied by a more pronounced $\zeta\text{-Fe}_2\text{O}_3$ phase fraction (10.7%) and a smaller contribution from Fe_3O_4 (10.6%), while the $\eta\text{-Fe}_2\text{O}_3$ phase (4.5%) and Fe_4O_5 (1.5%) remain subordinate. In contrast, a region enriched in Fe_4O_5 at (27, 4) shows a reduced Fe_5O_7 contribution (60.6%) and a significant Fe_4O_5 fraction (25.1%), together with a moderate $\eta\text{-Fe}_2\text{O}_3$ phase contribution (10.5%) and only minor Fe_3O_4 (3.9%). The $\zeta\text{-Fe}_2\text{O}_3$ phase contribution at this position is negligible and slightly negative due to background subtraction and normalization effects. Overall, these observations highlight the coexistence and spatial variability of multiple iron oxide phases at 64 GPa.

Reviewing the cake view of **80 GPa** shown in Fig. 5.23, it shows, that the initial HP $\theta\text{-Fe}_2\text{O}_3$ phase is prevalent as well as the HP/HT $\eta\text{-Fe}_2\text{O}_3$ phase. In addition, diffraction features corresponding to the higher iron oxides Fe_5O_7 and $\text{Fe}_{25}\text{O}_{32}$ can be identified, where the contribution from Fe_5O_7 is negligible.

The corresponding 2D-maps at 80 GPa are depicted in Fig. 5.24. Only minor contributions from the initial $\theta\text{-Fe}_2\text{O}_3$ phase are observed, while the HT $\eta\text{-Fe}_2\text{O}_3$ phase is present in slightly larger amounts. The dominant phase across the mapped region is $\text{Fe}_{25}\text{O}_{32}$, which is distributed broadly within the central part of the sample rather than being confined to a localized region.

As in the previous cases for a quantitative assesment, the reported values represent relative contributions of selected diffraction peaks and do not correspond to absolute phase abundances.

In a region dominated by the $\theta\text{-Fe}_2\text{O}_3$ phase at $(x, y) = (15, 5)$, this phase accounts for the majority of the signal (67.1%), accompanied by a smaller contribution from the $\eta\text{-Fe}_2\text{O}_3$ phase (18.1%) and $\text{Fe}_{25}\text{O}_{32}$ (14.8%). At a location associated with enhanced $\eta\text{-Fe}_2\text{O}_3$ phase contribution (9, 12), the $\eta\text{-Fe}_2\text{O}_3$ phase becomes dominant (62.2%), while the $\theta\text{-Fe}_2\text{O}_3$ phase (17.4%) and $\text{Fe}_{25}\text{O}_{32}$ (20.4%) contribute more moderately. In contrast, a region characterized by $\text{Fe}_{25}\text{O}_{32}$ at (12, 10) shows a strong dominance of this phase (82.4%), with only minor contributions from the $\eta\text{-Fe}_2\text{O}_3$ phase (15.0%) and a very small $\theta\text{-Fe}_2\text{O}_3$ phase fraction (2.6%). These results further emphasize the spatial heterogeneity of the phase assemblage at 80 GPa and support the interpretation of distinct stability fields for the observed iron oxide phases under these conditions.

An overview of for all maps, without a normalization in intensity, is provided in the Appendix in Fig. A.19 – Fig. A.21. Further, the integrated cakes are also provided in the Appendix in Fig. A.22 – Fig. A.24 as well as thr calculated power pattern in Fig. A.25 – Fig. A.27. The crystallographic files for rhenium and diamond are provided from Wyckoff [177]. $\alpha\text{-Fe}_2\text{O}_3$, $\iota\text{-Fe}_2\text{O}_3$, $\theta\text{-Fe}_2\text{O}_3$, $\eta\text{-Fe}_2\text{O}_3$, Fe_5O_7 , $\text{Fe}_{25}\text{O}_{32}$ files are from

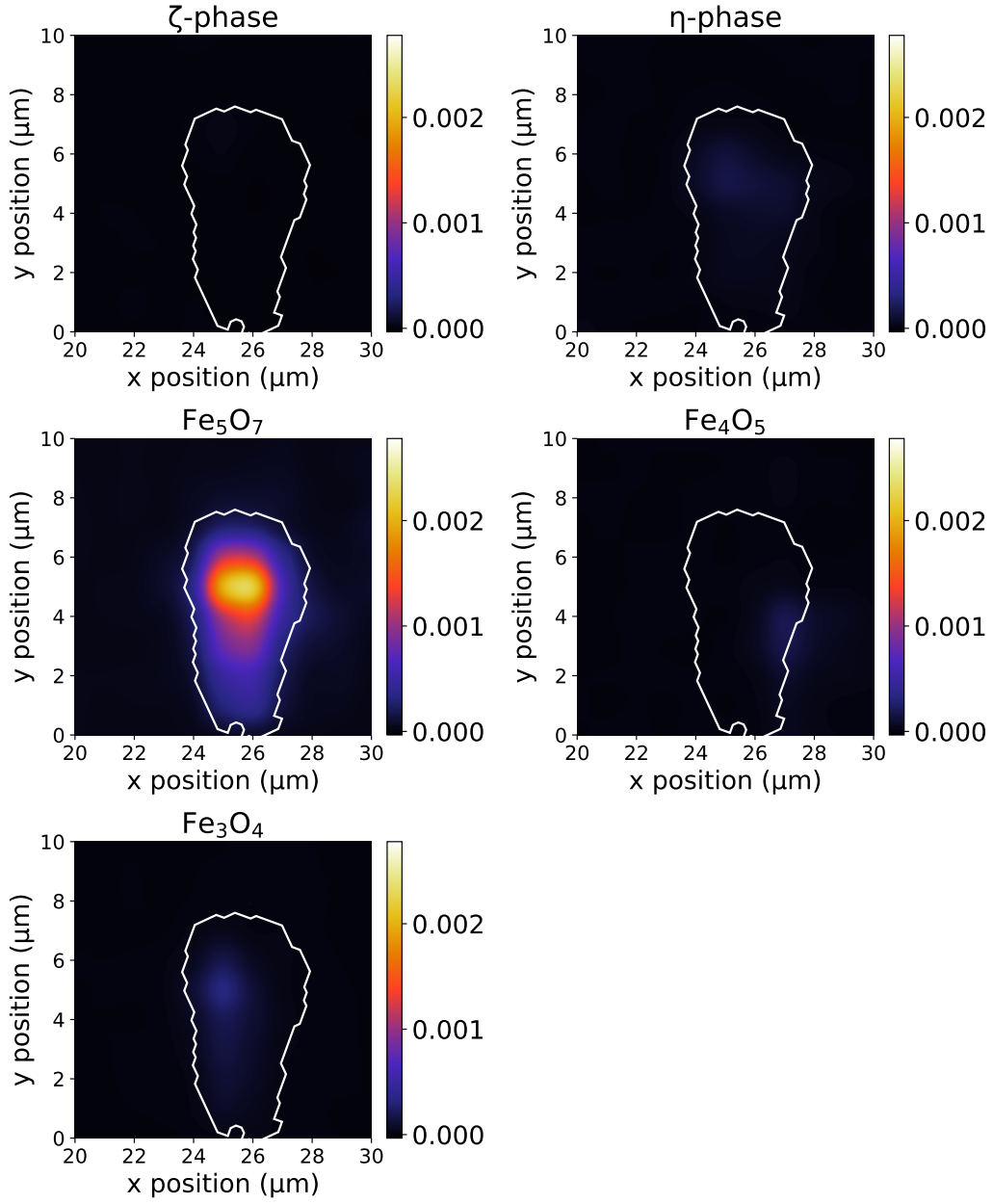


Figure 5.22: XRD-derived two-dimensional phase maps at 64 GPa with the white outline indicating the sample boundary. From left to right: $\zeta\text{-Fe}_2\text{O}_3$, $\eta\text{-Fe}_2\text{O}_3$, Fe_5O_7 , Fe_4O_5 , and Fe_3O_4 .

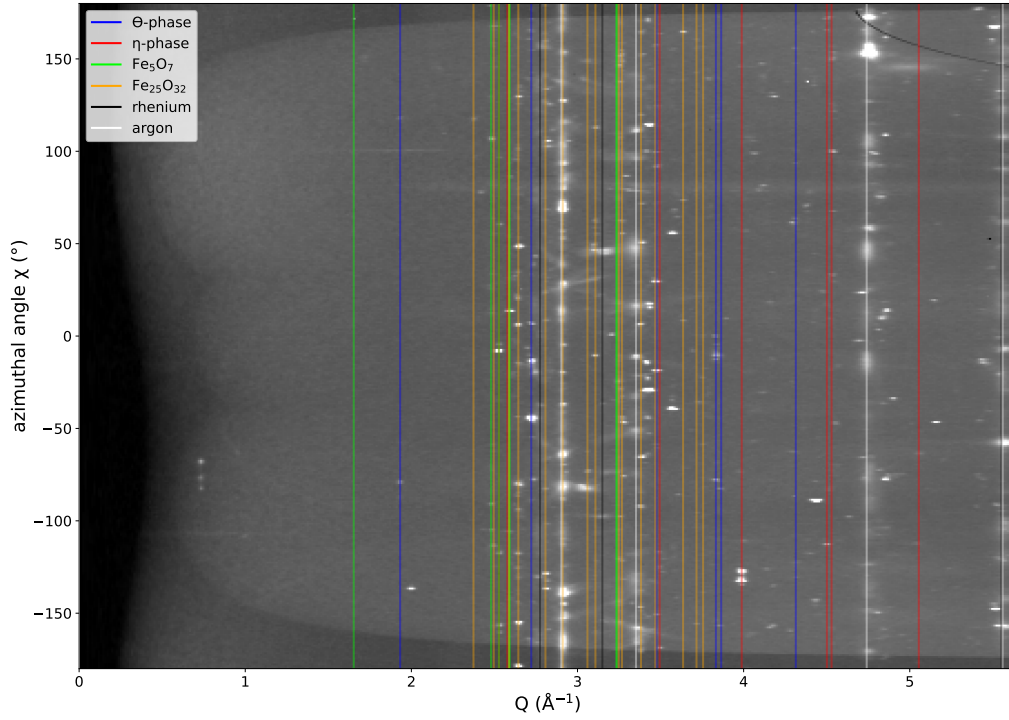


Figure 5.23: XRD cake view of image 179 at 80 GPa used for phase identification. The initial θ - Fe_2O_3 phase (blue), the HT phase η - Fe_2O_3 (red) are indicated, together with reflections from higher oxides Fe_5O_7 (green) and $\text{Fe}_{25}\text{O}_{32}$ (orange). Contributions from argon (white) and the rhenium gasket (black) are marked for completeness.

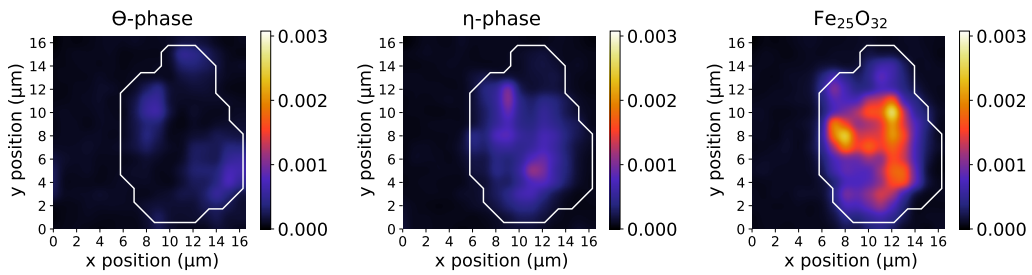


Figure 5.24: XRD-derived 2D phase maps at 80 GPa with the white outline representing the sample boundary. From left to right: θ - Fe_2O_3 , η - Fe_2O_3 and $\text{Fe}_{25}\text{O}_{32}$.

Bykova et al. [11] and $\zeta\text{-Fe}_2\text{O}_3$ was combined from Bykova et al. [11] and the doctoral thesis of Bykova [178]. The crystallographic files for Fe_4O_5 by woodland et al. [179], Fe_3O_4 by Ricolleau and Fei [180], $\delta\text{-Fe}_3\text{O}_4$ from Zurkowski et al. [181].

In summary, the XRD results show that increasing pressure in combination with laser heating promotes the formation of multiple higher iron oxides at 64 and 80 GPa, in contrast to the phase assemblage observed at 38 GPa. The initial Fe_2O_3 phases characteristic of each pressure point remain detectable but are present in comparatively low amounts after heating. For the experiments at 38 and 64 GPa, the spatial phase distributions allow identification of the laser-heated region. At higher pressures, Fe_5O_7 at 64 GPa and $\text{Fe}_{25}\text{O}_{32}$ at 80 GPa emerge as the dominant phases after laser heating and remain stable upon quenching.

To further correlate these structural observations with changes in the electronic structure and local bonding environment of iron, RXES measurements are presented in the following section.

5.5.3 Resonant X-ray emission spectroscopy

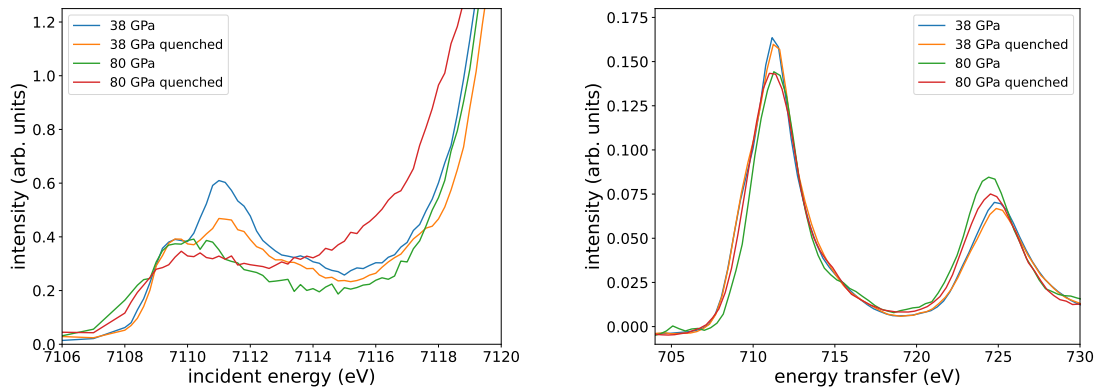


Figure 5.25: **Left)** spectra from the CEE cut, namely the HERFD-XANES spectra and **right)** spectra from CIE cut, with L-edge like information sum of two cuts (7109.2 to 7111.6 eV) and area normalized for the pressures at 38 and 80 GPa before heating and temperature quenched.

The results of the RXES measurements are presented in Figure 5.25 with the CEE cuts on the left side and CIE cuts on the right for all measurements taken. The corresponding RXES maps, CEE cuts and the single CIE cuts are in the Appendix A.7.4.

CEE – HERFD-XANES Inspection of the CEE cuts corresponding to the HERFD-XANES spectra (cf. Fig. 5.25, left) reveals distinct differences between each spectrum of the pre-edge region.

At **38 GPa** for $\alpha\text{-Fe}_2\text{O}_3$, a distinct pre-edge double-peak structure with the highest intensity is observed, with maxima at 7112.7 eV and 7114.2 eV. These features can be assigned to transitions into the 5T_2 and 5E_g states, respectively, reflecting the crystal-field splitting of the Fe 3d orbitals in a high-spin configuration. The presence of two clearly separated peaks is characteristic of Fe in a (near-)octahedral coordination environment, where the t_{2g} and e_g orbitals are energetically well separated.

After quenching, the features remain clearly visible, albeit with reduced intensity, indicating that the overall electronic structure and local coordination are largely preserved. The slight decrease in intensity suggests minor relaxation effects, namely less distortion, of the local structure upon heating and subsequent quenching.

Within the established framework of Fe K-edge XANES theory, an intense pre-edge feature reflects an enhanced 1s to 3d transition probability, which can increase through 3d-4p orbital mixing when local inversion symmetry is reduced [84, 92]. As discussed by Baker et al. [182], the intensity and shape of the pre-edge are strongly influenced by local symmetry and distortion: deviations from centrosymmetric coordination enhance 3d-4p hybridization and modify both the intensity and the spectral distribution of the pre-edge features [182].

At **80 GPa**, corresponding to the θ -Fe₂O₃ phase where the polyhedra are prisms, the pre-edge region shows a markedly different behavior. The distinct double-peak structure observed at 38 GPa is no longer resolved and instead appears as a broadened and less structured feature centered near ~ 7110 eV. This loss of clearly separated peaks indicates a modification of the ligand-field splitting and a redistribution of the Fe 3d-derived electronic states, consistent with changes in the local electronic structure and coordination environment [92].

The broadening and merging of the pre-edge features can be understood in terms of increased complexity of the local coordination environment. According to Baker et al. [182], lower-symmetry environments lead to a lifting of degeneracy of the 3d orbitals beyond the simple t_{2g}/e_g splitting, resulting in multiple closely spaced energy levels. The corresponding transitions overlap in energy and therefore appear as a single broadened feature rather than distinct peaks. In addition, increased distortion enhances 3d-4p mixing, which further redistributes spectral weight and contributes to the observed change in peak shape.

The quenched spectrum at 80 GPa shows a markedly enhanced intensity in the rising-edge region above approximately 7115 eV compared to the corresponding spectrum before heating, while the pre-edge region itself remains comparatively weak. At the same time, the pre-edge appears broader. This suggests the presence of multiple local coordination environments after quenching, leading to a superposition of different crystal-field splittings and therefore a more complex spectral shape, consistent with the mix of octahedra and prisms within this phase. As emphasized by Baker et al. [182], such behavior is typical for systems with increased structural disorder or coexistence of different local symmetries, where overlapping transitions produce broadened and less well-defined features.

Overall, the HERFD-XANES spectra reveal a systematic evolution with increasing pressure from 38 to 80 GPa, characterized by a broadening of the pre-edge feature and a redistribution of spectral weight toward lower incident energies. The suppression of the distinct 5E_g and 5T_2 features at elevated pressure indicates significant modifications of the local electronic structure, consistent with pressure-induced changes in Fe-O bond distances, coordination geometry, and metal-ligand hybridization [92]. Temperature effects introduced by laser heating further modify the relative spectral intensities. While the quenched spectra at 38 GPa largely preserve the overall pre-edge structure by retaining the distinction between 5E_g and 5T_2 states, changes in intensity indicate

partial relaxation to a more centrosymmetric environment [84]. At 80 GPa, temperature-quenched spectra lead to a pronounced enhancement of intensity in the rising-edge region also indicative of a fraction of Fe²⁺, whereas the pre-edge remains comparatively weak, implying a temperature-driven relaxation into a more centrosymmetric coordination upon quenching. Together, these observations demonstrate that both pressure and temperature influence the electronic structure, with pressure primarily governing the modification and broadening of pre-edge features and temperature affecting the relative spectral weight distribution.

CIE – L-edge like information

Tab. 5.5 summarizes the extracted L_3 and L_2 peak positions seen in Fig. 5.25 right) together with their uncertainties and the corresponding energy splittings extracted by fitting a Gaussian curve to each peak. The reported uncertainties correspond to the statistical errors obtained from the peak fitting procedure. They represent the formal fitting uncertainties. Additional systematic contributions, such as the spectrometer energy calibration and instrumental resolution, are not included in these values. The L_3 and L_2 peak positions were determined by fitting the respective features. For this purpose, a fitting window of ± 1.5 eV around the peak maximum was used.

In addition to the individual peak positions, the energy separation between the L_3 and L_2 features provides further information on the electronic structure. This splitting reflects the energetic separation of the corresponding $2p_{3/2}$ and $2p_{1/2}$ final states involved in the RXES process and is sensitive to changes in the local electronic environment of Fe. Variations in the L_3 - L_2 separation can therefore serve as an indicator of modifications in the Fe 3d electronic structure under compression. As established by Westre et al. [92], both the absolute energy positions and the splitting of these features are sensitive to oxidation state, ligand-field strength, and coordination environment, reflecting changes in the 3d electronic structure. As discussed by Baker et al. [182], additional effects such as changes in covalency and local symmetry can further influence both the absolute peak positions and their energetic separation through modifications of the $2p$ -3d interactions and the distribution of unoccupied electronic states [182].

At **38 GPa**, the CIE spectra display a pronounced and relatively sharp first peak (L_3) centered at 711.27 eV. This feature reflects well-defined Fe 3d-derived final states and indicates a comparatively narrow distribution of electronic energies. The sharpness of the peak suggests a relatively homogeneous local coordination environment with limited distortion. In the framework of Westre et al. [92], such well-defined features are characteristic of a high-spin Fe³⁺ configuration in a relatively symmetric coordination environment. After quenching, no significant energy shift is observed. Instead, a slight reduction in intensity is apparent, while the peak width remains nearly unchanged. This suggests that the overall electronic configuration is largely preserved upon heating and quenching, with only minor modifications to the local structure. A comparable behavior is observed for the L_2 peak.

The energy separation between the L_3 and L_2 peaks amounts to 13.72 eV (cf. Tab. 5.5). After quenching, this splitting remains nearly unchanged at 13.71 eV, indicating that the overall electronic structure is largely preserved. Within the framework described by Westre et al. [92], this stability suggests that neither the oxidation state nor the ligand-field strength is significantly altered by the thermal treatment at this pressure,

while Baker et al. [182] further indicate that no substantial change in covalency or symmetry occurs.

For **80 GPa**, corresponding to the predominantly LS state, clear modifications of the spectral shape and peak positions are observed. The L_3 peak shifts to higher energy (711.47 eV) compared to 38 GPa, while the L_2 peak shifts to lower energy transfer (724.46 eV), resulting in a reduced energy separation. In addition, a slight broadening of the spectral features is observed, indicating a wider distribution of electronic states. According to Westre et al. [92], such shifts in peak position are indicative of changes in the ligand-field strength and electronic configuration, while Baker et al. [182] attribute the observed broadening to increased structural distortion and enhanced mixing of electronic states, leading to a redistribution of spectral weight.

The energy splitting decreases to 12.99 eV, representing the minimum value observed in this dataset. After temperature quenching, the splitting increases again to 13.28 eV. This reversible behavior indicates that the electronic structure is sensitive to temperature-induced changes and partially recovers upon quenching. A reduced splitting is associated with a LS state, whereas larger splittings correspond to HS states [92]. The increase in splitting after quenching therefore suggests a partial restoration of a HS state or a reduction in distortion.

While the absolute spectral intensity varies between the different pressure conditions, it functions as indicator of the prevailing spin state. In contrast, the evolution of the L_3 - L_2 energy splitting shows a clearer and more systematic trend. A reduced splitting is associated with the LS state, whereas larger splittings correspond to HS conditions. This interpretation is consistent with the XES results presented beforehand and supported by both Westre et al. [92] and Baker et al. [182], where changes in electronic configuration, ligand-field strength, hybridization, and symmetry collectively influence the observed spectral features.

Overall, the observed evolution of the L_3 and L_2 features reflects a pressure-induced modification of the Fe electronic structure, involving changes in spin state, ligand-field interactions, oxidation state, and local symmetry. The combination of peak shifts, intensity variations, and changes in energy splitting provides a consistent picture of the electronic transitions occurring under compression.

Table 5.5: L_3 and L_2 peak positions with corresponding errors and energy differences.

Sample	L_3 (eV)	error (eV)	L_2 (eV)	error (eV)	ΔE (eV)
38 GPa	711.27	0.06	724.99	0.22	13.72
38 GPa quenched	711.31	0.05	725.02	0.22	13.71
80 GPa	711.47	0.05	724.46	0.14	12.99
80 GPa quenched	711.34	0.05	724.62	0.14	13.28

5.6 Discussion

In the following, these results are discussed in the context of previous room-temperature and static compression studies, with particular emphasis on the role of mixed-spin-states, the influence of temperature on the development of the spin transition, and their

implications for the behavior of ferric iron along the lower-mantle adiabatic temperature profile [10].

5.6.1 Electronic and structural behavior

The IAD values obtained from the $\text{K}\beta$ XES spectra are summarized in Fig. 5.26, which additionally includes data from previous experiments to establish a continuous pressure evolution. Triangles indicate the measurements obtained during the present HP/HT experiments, while circles and squares correspond to earlier room-temperature measurements [161]. The colored background regions denote the pressure stability fields of the different Fe_2O_3 polymorphs, which partly overlap due to uncertainties reported in the literature.

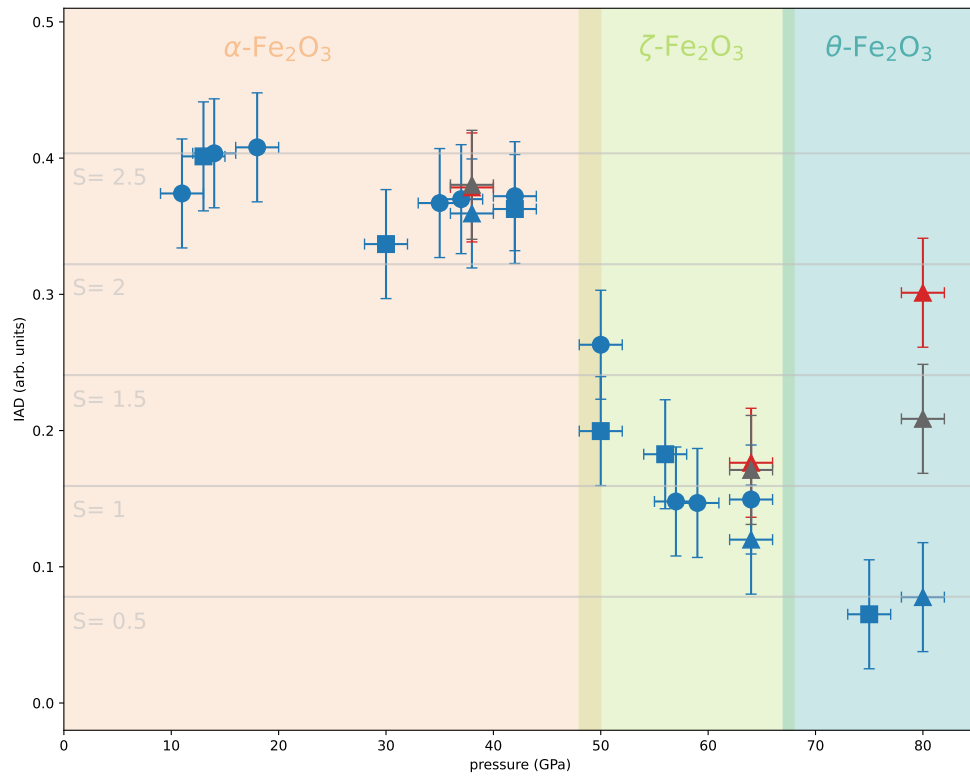


Figure 5.26: IAD values against pressure including different experiments. Blue values marks cold compressed, red values are obtained during heating and grey values represent temperature quenched measurements. Circles mark measurements from experiments in 2020, whereas squares stem from an experiment in June 2022 and triangles are from an experiment in November 2022. The colored areas indicate the prevalent phases, which are overlapping due to uncertainties from the literature. Data points marked by circles and squares are published by Albers et al. [161].

The low-pressure regime is exemplified by measurements conducted at **38 GPa**, where the IAD values obtained under cold compression and during laser heating agree well with previous experiments [161] and consistently present the HS state of Fe^{3+} in Fe_2O_3 . The slight increase in IAD observed upon heating and subsequent quenching remains within experimental uncertainty and therefore does not provide evidence for a pressure-

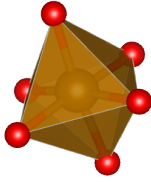
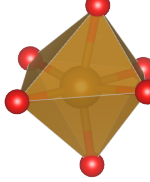
or temperature-induced spin crossover at this pressure. Nevertheless, it might reflect structural changes, which are for example observable in FeO [146].

Despite the apparent electronic stability, observable as a stable spin state, inferred from XES, XRD analysis reveals the coexistence of the α -Fe₂O₃ phase with a dominant contribution ($\sim 78\%$ central in the heating spot) from the ι -Fe₂O₃ polymorph. The persistence of a HS signature in the XES data therefore implies that Fe³⁺ remains predominantly in the HS configuration in both structural polymorphs. Additionally, L-edge-like information extracted from the CIE cuts indicates only minor differences between the phases, which remain negligible within experimental uncertainty. In contrast, the HERFD-XANES derived from the CEE cuts exhibits more pronounced intensity variations; however, the overall spectral shape remains unchanged, pointing to similar local electronic and structural environments around Fe.

The polyhedral volume of the α - and ι -Fe₂O₃ phase in Tab. 5.6, used for calculating the spin of both phases support the IAD findings of being in HS state. The threshold at which the polyhedral volume indicates a change in spin-state is based on the experimentally established correlation between Fe³⁺ spin configuration and FeO₆ octahedral volume reported by Vasiukov et al. [183]. In that study, a systematic analysis of Fe³⁺-bearing compounds demonstrated that spin pairing in octahedral Fe³⁺ occurs when the FeO₆ polyhedral volume is compressed below a critical value of approximately 8.9-9.1 Å³, reflecting the crystal-field stabilization of the LS configuration at reduced metal-ligand distances. Above this threshold, Fe³⁺ remains in the HS state. The polyhedral volumes determined for the α - and ι -Fe₂O₃ phases at 38 GPa remain well above this critical range, consistent with the HS state inferred from the IAD analysis. Thus, the structural data independently support the spectroscopic observation that Fe³⁺ does not undergo spin crossover at this pressure.

Therefore, at a pressure of 38 GPa and after heating up to 2020 K, corresponding to a depth of ~ 1000 km in the Earth, ι -Fe₂O₃ as the dominant phase is in HS state.

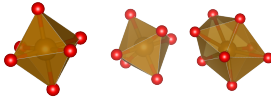
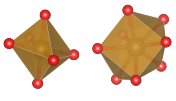
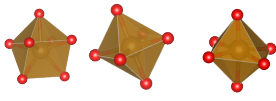
Table 5.6: Polyhedral and spin-state parameters for the α - and ι -Fe₂O₃ phases.

	α -Fe ₂ O ₃	ι -Fe ₂ O ₃
polyhedron		
polyhedra per unit cell (ppuc)	24	8
volume (Å ³)	24×9.18 (HS)	8×9.30 (HS)
calculated spin	2.5	2.5

The intermediate-pressure regime around **64 GPa** corresponds to a plateau within the first step of the two-stage spin crossover in Fe₂O₃. Compared to the HS regime at lower pressures, the K $\beta_{1,3}$ XES IAD assumes intermediate values, indicating that the iron no longer exists in a purely HS configuration but instead reflects a mixed-spin regime in which HS and LS Fe³⁺ coexist in two different sites.

Upon laser heating at 64 GPa, the IAD increases beyond the experimental uncertainty, indicating higher spin values. After quenching, the IAD decreases again but remains within the intermediate range characteristic of the mixed-spin regime. These systematic variations demonstrate that the local electronic configuration is sensitive to temperature and phase evolution at this pressure, suggesting that additional HS contributions are introduced during heating, potentially through the formation of mixed-valence phases.

Table 5.7: Polyhedral volumes and calculated spin-states for the ζ -, η - Fe_2O_3 , and Fe_5O_7 phases. Calculation are based on assuming solely ferric iron and for octahedral coordination.

	$\zeta\text{-Fe}_2\text{O}_3$	$\eta\text{-Fe}_2\text{O}_3$	Fe_5O_7
polyhedra			
ppuc	21	21	22
volume ($\text{\AA}^3$)	6×15.40 (HS) 9×8.62 (LS) 6×7.52 (LS)	6×15.24 (HS) 15×8.40 (LS)	6×10.87 (HS) 10×8.59 (LS) 6×8.54 (LS)
calculated spin	1.07	1.07	0.95

Structural information obtained from XRD reveals that the sample undergoes substantial phase complexity in this pressure regime. After laser heating, the diffraction patterns indicate the coexistence of several iron oxide phases, including ζ - and η - Fe_2O_3 , Fe_4O_5 , Fe_3O_4 , and Fe_5O_7 , with Fe_5O_7 forming the dominant contribution in the heated assemblage with around 80 % in the heating spot. The simultaneous presence of these phases demonstrates that the electronic response recorded by XES cannot be uniquely attributed to a single polymorph.

To evaluate whether the observed spin-state evolution can be explained solely by structural compression, the polyhedral-volume criterion proposed by Vasiukov et al. [183] was applied to the most abundant structures identified by XRD. This empirical approach relates the spin-state of Fe^{3+} to the volume of its coordination polyhedron, with smaller volumes generally corresponding to LS configurations. Application of this model to the ζ - Fe_2O_3 structure indicates that the two octahedral Fe sites, with volumes of approximately 8.6 and 7.5 $\text{\AA}^3$, fall within the LS regime, while a HS contribution is associated with the larger trigonal-prismatic polyhedron. Using the site multiplicities derived from the triclinic structure yields an average calculated spin-state of

$$S_{\text{calc}} = \frac{(6 \times 2.5) + (9 \times 0.5) + (6 \times 0.5)}{21} \approx 1.07, \quad (5.4)$$

consistent with a mixed-spin also observable in the IAD values. A similar calculation for Fe_5O_7 yields an average spin value of approximately 0.95 with four Fe^{3+} and one Fe^{2+} (Tab. 5.7). This result does not reproduce the experimentally observed evolution of the IAD exactly, particularly the increase observed after heating. However, the difference is small and may be reflecting more structural changes than changes in spin.

This discrepancy shows the limitations of assigning spin-states solely on the basis of polyhedral volumes in the crossover regime. The polyhedral-volume criterion of Vasiukov et al. [183] was developed for Fe^{3+} in octahedral coordination and therefore provides only a semi-quantitative guide in the present system, where mixed coordinations and mixed valence contribute significantly to the observed electronic signal.

A similar limitation arises when applying Fe-O bond-length systematics as a structural proxy for spin-state assignment. Previous studies have shown that octahedrally coordinated Fe^{3+} approaches the LS configuration when the average Fe-O bond distance contracts to values near or below $\sim 1.9 \text{ \AA}$ [184]. Application of this empirical threshold to the present structures broadly supports the polyhedral-volume trends. However, the FeO_6 octahedra observed at these pressures are distorted and exhibit a wide distribution of individual Fe-O bond lengths that may span both sides of the proposed threshold within a single polyhedron. As a consequence, assigning spin-states based on individual bond lengths can systematically overestimate the HS fraction and does not yield a quantitative average spin-state directly comparable to the XES-derived IAD values.

As the main component after temperature-quenching is Fe_5O_7 , it influences the measured spin the most, but also introduces significant mixed-valence character into the system. In its crystallographic description, Fe_5O_7 contains both Fe^{3+} and Fe^{2+} sites. High-pressure single-crystal X-ray diffraction studies by Khandarkhaeva et al. [12] show that the two octahedrally coordinated Fe^{3+} sites undergo a HS-LS crossover between approximately 43 and 51 GPa, whereas the trigonal-prismatic Fe^{2+} site remains in the HS configuration to at least 80 GPa. Consequently, Fe_5O_7 constitutes an intrinsically mixed-spin system at the pressures investigated here.

The presence of Fe^{2+} has important consequences for interpreting the XES data. Because Fe^{2+} possesses a larger ionic radius than Fe^{3+} in comparable coordination environments, its coordination polyhedra remain comparatively expanded even under strong compression. As a result, polyhedral volumes associated with Fe^{2+} sites are systematically larger than those of Fe^{3+}O_6 octahedra that have already entered the LS regime. Since polyhedral-volume criteria are calibrated primarily for Fe^{3+}O_6 environments, they cannot be directly transferred to a mixed-valence assemblage containing substantial Fe^{2+} and non-octahedral coordination.

This structural and valence complexity provides an explanation for the observed IAD evolution at 64 GPa. Despite the transformation from predominantly $\zeta\text{-Fe}_2\text{O}_3$ before heating to a Fe_5O_7 -dominated assemblage after heating, the average spin moment inferred from XES increases, possibly due to the structural changes. Although part of Fe_5O_7 is reduced to Fe^{2+} , the ferrous iron contains its HS state, whereas the two ferric octahedral sites have already entered the LS regime.

In addition, contributions from other coexisting phases identified by XRD, such as Fe_3O_4 , Fe_4O_5 , and $\eta\text{-Fe}_2\text{O}_3$, further influence the average spin-state. This highlights that considering only the dominant phase is insufficient for a quantitative description of the spin-state evolution.

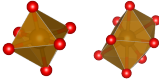
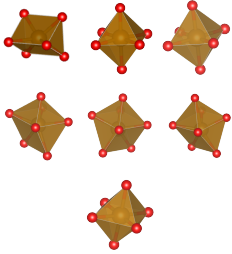
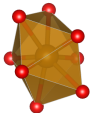
Taken together, these observations demonstrate that the spin crossover in Fe_2O_3 around 64 GPa occurs within an extended mixed-spin regime in which the average spin-state is controlled not only by local compression of FeO_6 polyhedra but also by the evolving phase assemblage, coordination topology, and valence distribution. Under these conditions,

the $\text{K}\beta_{1,3}$ XES IAD analysis provides the most direct experimental constraint on the average Fe spin-state. However, at a pressure of 64 GPa and temperatures up to 2190 K, corresponding to a depth of around 1500 km in the Earth, mixed-spin-states dominate. Additionally, reduction and oxidation states are changing towards higher oxides like Fe_5O_7 , under the release of oxygen, with Fe^{2+} and Fe^{3+} sites.

At **80 GPa**, the evolution of the IAD differs markedly from the behavior observed at lower pressures and reflects a fundamentally different electronic and structural regime. Prior to laser heating, the IAD indicates that iron resides in a LS configuration. Upon heating, the IAD increases significantly, before decreasing again after temperature quenching to values characteristic of a mixed-spin-state. This evolution cannot be explained by a simple continuation of the ferric spin crossover observed at intermediate pressures.

At these conditions, laser heating induces the formation of $\text{Fe}_{25}\text{O}_{32}$, a mixed valenced iron oxide with a complex crystal structure. High-pressure single-crystal XRD studies show that $\text{Fe}_{25}\text{O}_{32}$ does not exhibit a pressure-induced spin crossover within the investigated pressure range. Instead, its compression behavior is smooth and continuous, without abrupt changes in polyhedral volumes or compressibility that would indicate a HS-LS transition [12]. This contrasts with Fe_2O_3 polymorphs and Fe_5O_7 , where pronounced volume changes accompany ferric spin pairing.

Table 5.8: Polyhedral volumes and calculated spin-states for the θ -, η - Fe_2O_3 , $\text{Fe}_{25}\text{O}_{32}$ (calculation are based on assuming solely ferric iron and for octahedral coordination), and δ - Fe_3O_4 phases.

	θ - Fe_2O_3	η - Fe_2O_3	$\text{Fe}_{25}\text{O}_{32}$	δ - Fe_3O_4
polyhedra				
ppuc	8	21	55	18
V ($\text{\AA}^3$)	8×6.01 (LS)	6×13.02 (HS) 15×7.18 (LS)	6×11.11 (HS) 5×10.94 (HS) 6×10.66 (HS) 10×8.01 (LS) 10×7.90 (LS) 10×7.50 (LS) 8×6.77 (LS)	18×14.31 (HS)
calc. spin	0.5	1.07	1.19	2.33

The spin for $\text{Fe}_{25}\text{O}_{32}$ would result in a calculated spin of 1.12, if assumed, that only ferric iron is present. When ferrous iron is taken into account the calculation is as follows:

$$S_{\text{calc}} = \frac{(0.8 \times 2.5) + (30 \times 0.5) + (17 \times 2) + (7.2 \times 0)}{55} \approx 1.19, \quad (5.5)$$

This behavior highlights that spin crossover in ferric iron oxides is not solely controlled by pressure, but depends sensitively on local coordination geometry and structural environment.

Analysis of the polyhedral volumes in $\theta\text{-Fe}_2\text{O}_3$ (cf. Tab. 5.8) indicates that iron is expected to reside in a LS state prior to heating, consistent with the observed low IAD. However, the strongly increased IAD during heating cannot be explained by $\theta\text{-Fe}_2\text{O}_3$ or $\text{Fe}_{25}\text{O}_{32}$ alone. Instead, it is most plausibly attributed to the transient formation of $\delta\text{-Fe}_3\text{O}_4$, which is stable only at HP and HT ($>\approx 75$ GPa, $>\approx 2000$ K) and is known to host iron in the HS state [12, 185, 186].

The heated assemblage therefore likely consists of a mixture of phases with distinct spin-states. The elevated IAD during heating may reflect the dominant contribution of HS iron associated with transient $\delta\text{-Fe}_3\text{O}_4$, in combination with coexisting phases such as $\eta\text{-Fe}_2\text{O}_3$ and $\text{Fe}_{25}\text{O}_{32}$, rather than a reversal of the ferric spin crossover. Also possible is another component, which undergoes a transition to HS at HT, which could not be assigned unambiguously in the XRD data due to its complexity.

Upon quenching, the IAD decreases and shows $\text{Fe}_{25}\text{O}_{32}$ in XRD, which forms from Fe_3O_4 at high pressure and temperature [11]. The resulting mixed-phase assemblage, dominated by $\text{Fe}_{25}\text{O}_{32}$ with minor contributions from other oxides, yields an intermediate spin signature consistent with a mixed-spin-state.

Notably, RXES spectra collected before and after heating at 80 GPa do not exhibit pronounced qualitative differences. This indicates that the observed electronic changes primarily reflect variations in phase proportions and spin-state contributions, rather than fundamental modifications of the local electronic structure within a single phase.

Taken together, these observations at conditions at 80 GPa and temperatures up to 2470 K correspond to around 1800 km depth in the Earth suggest a transformation pathway in which $\theta\text{-Fe}_2\text{O}_3$ evolves into $\delta\text{-Fe}_3\text{O}_4$ at high temperature, followed by stabilization of $\text{Fe}_{25}\text{O}_{32}$ upon quenching. The electronic response at 80 GPa is therefore governed by phase evolution and mixed-spin assemblages, rather than by a pressure and/or temperature-induced spin crossover of ferric iron alone. Additionally despite ferric iron as a cold compressed starting material, along the Earth's adiabatic temperature profile [10] ferrous iron as well as free oxygen are present.

The measured data points are filled into the phase diagram in Fig. 5.27. When temperature-quenched not primarily $\eta\text{-Fe}_2\text{O}_3$ is found, but instead Fe_5O_7 at 64 GPa and $\text{Fe}_{25}\text{O}_{32}$ at 80 GPa.

In the following, these findings are placed in the context of previous experimental and theoretical studies to assess their consistency with earlier interpretations and to highlight the new constraints provided by combined *in situ* XES, RXES, and XRD measurements.

5.6.2 Comparison to other studies

The present dataset provides an internally consistent link between the evolution of the Fe spin-state derived from $\text{K}\beta$ XES (IAD), complementary electronic fingerprints from K-edge RXES (CEE and CIE cuts), and phase identification from XRD after heating.

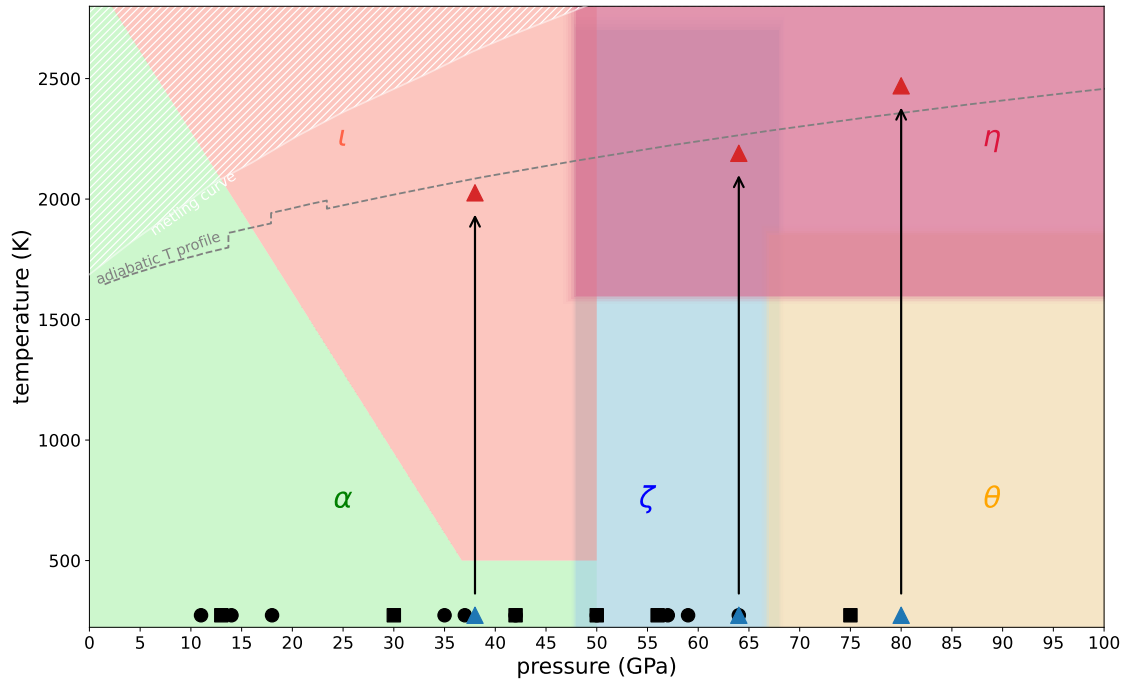


Figure 5.27: Phase stability fields of Fe_2O_3 from Fig. 5.1 including measured data points from different experiments (black). Blue values marks cold compressed, red values are obtained during heating. Circles mark measurements from experiments in 2020, whereas squares stem from an experiment in June 2022 and are already published in Albers et al. [161] and triangles represent the experiment in November 2022. Modified after Bykova et al. [11] with boundaries also from Ito et al. [51] and Albers et al. [161], the adiabatic temperature profile from Katsura et al. [10], and FeO melting curve as a proxy from Morard et al. [166].

This combined approach allows key ambiguities in the Fe_2O_3 literature to be addressed, in particular the relationship between spin-state evolution, structural transformations, and phase assemblages under HP and HT conditions.

At 38 GPa, XES indicates a robust HS state before, during, and after heating, while XRD reveals coexistence of α - and ι - Fe_2O_3 after heating. This behavior is consistent with early diffraction work that emphasized structural transformations as a function of compression and temperature, but lacked a direct electronic probe [49, 153, 156, 157]. In particular, the formation of ι - Fe_2O_3 at moderate pressures upon heating aligns with the broadly observed tendency of Fe_2O_3 to access $\text{Rh}_2\text{O}_3(\text{II})$ -related topologies at elevated temperature [11, 51, 154, 155]. The crucial additional constraint from the present study is that the emergence of ι at 38 GPa does not require an accompanying spin collapse: within uncertainty, the $\text{K}\beta'$ intensity and IAD remain essentially constant. This is consistent with the decoupling of crystallographic and electronic transitions reported for Fe_2O_3 , indicating that structural changes alone do not uniquely determine the spin-state [41].

Room-temperature compression studies generally place the onset of a major transformation in Fe_2O_3 between ~ 45 and 60 GPa, accompanied by a $\sim 10\%$ volume collapse and a progressive loss of magnetism [153–155]. In particular, Albers et al. [161] demonstrated using high-resolution $\text{K}\beta$ XES and $1s2p$ RXES that Fe_2O_3 undergoes a two-step spin transition: an initial reduction of the average spin-state between ~ 46 and 57 GPa associated with the α - to ζ -phase transformation, followed by a further decrease toward 75 GPa with the emergence of the θ -phase. Importantly, they reported an intermediate IAD plateau at approximately 40% of the HS reference value, which they attributed to a mixed-spin configuration arising from two inequivalent Fe sites in the ζ -phase.

The present results are fully consistent with this extended crossover picture. At 64 GPa, the IAD values likewise indicate a mixed-spin-state, and the temperature-induced increase in IAD demonstrates that the spin-state is not fully stabilized but can still redistribute under changing conditions. In addition, the CIE analysis provides complementary insight: compared to 38 GPa, the L_3 feature at 64 GPa is broadened and reduced in intensity, indicating a modification of the Fe $3d$ electronic states. This behavior is consistent with the loss of well-resolved, localized $3d$ excitations reported by Albers et al. [161] in the ζ -phase, where CEE and CIE cuts evolve from discrete ${}^5T_{2g}/{}^5E_g$ transitions toward a more dispersive, continuum-like character. While the present measurements do not resolve individual crystallographic sites, the observed changes in intensity and line shape are compatible with a heterogeneous, site-dependent electronic response in the crossover regime.

A further important aspect of Albers et al. [161] is their discussion of the 40% IAD plateau, which deviates from the 50% value expected if only one of two equally abundant sites were to undergo a complete HS-LS transition. They attribute this discrepancy to symmetry reduction and line-shape modifications of the remaining HS site. In this context, the present analysis based on polyhedral volumes provides a structurally resolved complement: by evaluating each crystallographic Fe site individually, it enables a more quantitative assessment of mixed-spin configurations beyond the simplified equal-site expectation derived purely from electronic arguments.

At 80 GPa, the pre-heating spectrum is in LS state, consistent with the expectation that ferric spin pairing becomes dominant at sufficiently high compression [154, 158,

161]. Albers et al. [161] likewise observe a further reduction in IAD toward their highest pressures, associated with the θ -phase. The present dataset continues the LS state of $\theta\text{-Fe}_2\text{O}_3$ at cold compression and further demonstrates that heating at these conditions strongly modifies the electronic signal: the pronounced increase in IAD during heating and its partial retention after quenching coincide with the formation of mixed-valence higher order oxides (dominantly $\text{Fe}_{25}\text{O}_{32}$) after temperature-quenching. This extends the interpretation of the HP LS regime by showing that along adiabatic temperature profile-like paths, the measured spin-state may reflect a multiphase assemblage rather than a single ferric polymorph.

This observation helps rationalize discrepancies between studies that relied on a single probe or on quenched products alone. Interpretations that attribute HT magnetic signatures solely to structural transitions within Fe_2O_3 polymorphs [152] may be incomplete if mixed-valence assemblages are present but unresolved. Conversely, diffraction-based phase diagrams [11] did not always include an *in situ* electronic probe capable of tracking spin redistribution during transformation. The combined spectroscopic and diffraction constraints in the present study therefore reinforce the view that spin crossover, structural transition, and chemical re-equilibration are closely intertwined under HP/HT conditions.

A persistent theme in the Fe_2O_3 literature is that transformation pressures and inferred electronic transitions depend strongly on whether the sample is cold-compressed, annealed, or measured *in situ* at HT [11, 41, 51]. The present experiments emphasize that path dependence extends beyond purely structural effects: at 64 and 80 GPa, heating not only influences the spin but also drives chemical reorganization into higher order oxides or vice versa. This introduces an additional kinetic degree of freedom, redox and stoichiometric equilibration, that can dominate the observable spin signature. Consequently, reported variations in spin-transition pressures likely reflect differences in experimental conditions, in particular the pressure-temperature path and the degree of chemical equilibration.

Overall, the present results support a unified interpretation in which Fe_2O_3 exhibits HS stability to at least ~ 40 GPa even across α - to $\iota\text{-Fe}_2\text{O}_3$ transformations, an extended and heterogeneous crossover regime at intermediate pressures consistent with the two-step transition reported by Albers et al. [161], and LS-dominated ferric behavior at the highest pressures under cold conditions. Along adiabatic temperature profile relevant paths, however, heating readily accesses multiphase, mixed-valence assemblages (Fe_5O_7 , $\text{Fe}_{25}\text{O}_{32}$, and minor $\text{Fe}_3\text{O}_4/\text{Fe}_4\text{O}_5$), which can enhance HS spectral weight even when ferric sites are partly spin-paired compared to $\theta\text{-Fe}_2\text{O}_3$. The central new constraint provided here is therefore not a revised single boundary, but a phase-assemblage-based interpretation of spin signatures at lower-mantle conditions, highlighting that the measured spin-state often reflects a dynamically evolving iron-oxide assemblage rather than a single equilibrium Fe_2O_3 phase.

5.6.3 Geophysical implication

The combined electronic and structural results obtained in this study have direct implications for the behavior of ferric iron under lower-mantle conditions and for the interpretation of geophysical observations sensitive to density, elasticity, and electrical transport. In particular, the extended and heterogeneous nature of the spin crossover in

Fe_2O_3 , together with the formation of mixed-valence iron oxides at high pressure and temperature, suggests that ferric iron contributes to lower-mantle properties in a far more complex manner than implied by simplified phase or spin-transition models.

A key outcome of this study is that temperature does not merely modulate the ferric spin-state within a fixed Fe_2O_3 framework, but actively promotes mixed-valence iron oxides such as Fe_5O_7 and $\text{Fe}_{25}\text{O}_{32}$ at pressures of 64 and 80 GPa. Along a realistic mantle geotherm, such transformations are expected to be kinetically accessible over geological timescales. This implies that ferric iron introduced into the deep mantle e.g., via subducted, oxidized lithologies, may not persist exclusively as Fe_2O_3 polymorphs, but may redistribute into a spectrum of iron-rich oxides with distinct electronic and structural properties.

The formation of mixed-valence phases has important implications for redox buffering in the deep mantle. Phases such as Fe_5O_7 and $\text{Fe}_{25}\text{O}_{32}$ form under the release of oxygen and accommodate both Fe^{2+} and Fe^{3+} in well-defined crystallographic sites, enabling internal charge redistribution. This provides an efficient mechanism for stabilizing redox heterogeneity at depth and suggests that local oxygen fugacity in the lower mantle may be buffered by solid-state phase equilibria rather than by melt or fluid phases alone.

The spectroscopic evidence for mixed-spin and mixed-valence assemblages at HP/HT also bears directly on the interpretation of lower-mantle electrical conductivity. Experimental studies on iron-rich oxides such as Fe_4O_5 , Fe_5O_6 , and Fe_7O_9 have demonstrated strongly pressure-dependent conductivity increases up to at least ~ 60 GPa, without a transition to a fully metallic state [187].

Finally, the demonstrated sensitivity of iron spin-state and phase assemblage to temperature highlights the importance of kinetic and path-dependent effects in the deep mantle. Unlike laboratory cold-compression experiments, mantle materials experience prolonged heating at high pressure, allowing phase transformations and redox redistribution to proceed toward equilibrium. The persistence of mixed-spin signatures in quenched samples in this study indicates that such equilibrated states are not transient artifacts, but represent stable or metastable configurations relevant to geological timescales.

In addition, the observed spin-state and valence variability has direct implications for element partitioning in the lower mantle. Changes in spin-state modify the ionic radius and crystal-field stabilization of Fe, thereby influencing its site preference and exchange equilibria with other cations such as Mg. In particular, the transition from HS to LS Fe^{3+} in octahedral coordination is associated with a reduction in ionic radius, which can alter Fe-Mg partitioning between coexisting mineral phases. Experimental studies have demonstrated that iron partitioning between bridgmanite and ferropericlase is strongly controlled by both spin and valence state, with significant redistribution of iron occurring above ~ 70 GPa due to coupled changes in $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios and spin transitions [188].

In contrast, the persistence of HS Fe^{2+} in non-octahedral coordination, as observed in phases such as Fe_5O_7 , introduces locally expanded sites that may preferentially accommodate larger cations. As a consequence, the formation of mixed-valence iron oxides at high pressure and temperature may lead to a redistribution of major elements between phases, potentially modifying bulk composition and density contrasts in lower-mantle assemblages. As a consequence, the formation of mixed-valence iron oxides at

HP/HT may redistribute major elements between phases, potentially modifying bulk composition and density of subducted materials. [188].

A particularly important geodynamic implication arises in the context of subducted BIFs, which represent a major reservoir of ferric iron in the Earth's crust. During subduction to lower-mantle depths, iron oxides such as Fe_2O_3 and Fe_3O_4 are expected to undergo extensive phase transformations and chemical reactions under HP/HT conditions. As Fe_2O_3 can decompose at pressures above ~ 60 GPa to form mixed-valence phases such as Fe_5O_7 , this process is accompanied by the release of oxygen. This process represents a potential deep-mantle oxygen source, with estimates suggesting that subducted BIF material could generate significant amounts of free oxygen, sufficient to locally modify oxidation conditions in the surrounding mantle [189].

The presence of such oxygen-rich fluids or locally oxidizing environments may promote the conversion of Fe^{2+} to Fe^{3+} in mantle minerals, thereby shifting redox equilibria and influencing element partitioning, phase stability, and melting relations. In this context, the formation of higher iron oxides such as Fe_5O_7 and $\text{Fe}_{25}\text{O}_{32}$ provides a direct link between subducted surface materials and deep-mantle redox heterogeneity, highlighting the active role of iron oxides in the recycling of oxygen and the chemical evolution of the Earth's interior [189].

The combined electronic and structural results obtained in this study have direct implications for the behavior of ferric iron under lower-mantle conditions and for the interpretation of geophysical observations sensitive to density, elasticity, and electrical transport. Fe-bearing systems evolve through coupled spin, structural, and chemical pathways that depend on pressure, temperature, and bulk composition. Mixed-valence iron oxides such as Fe_5O_7 and $\text{Fe}_{25}\text{O}_{32}$ emerge as important endmember phases that constrain the limits of ferric spin crossover and provide new perspectives on density, elasticity, conductivity, and redox processes in the deep Earth.

In this context, the present study underscores the necessity of integrating *in situ* electronic probes with structural characterization when assessing the geophysical role of iron at lower-mantle conditions. Only by considering the full phase assemblage and its electronic heterogeneity can the macroscopic properties of deep Earth materials be reliably linked to their microscopic behavior.

5.6.4 Conclusion

This study combines *in situ* XES, RXES, and temperature-quenched XRD to investigate the coupled electronic and structural evolution of Fe_2O_3 under HP/HT conditions representative of the Earth's lower mantle. By linking spin-state information derived from $\text{K}\beta_{1,3}$ XES with crystallographic constraints from diffraction and polyhedral volume analysis, a consistent framework is established that relates pressure- and temperature-induced electronic transitions in ferric iron to changes in local bonding geometry, crystal symmetry, and phase stability. The results demonstrate that spin crossover, structural transformations, and associated density changes are not independent processes, but instead evolve in a coupled and continuous manner along geothermally relevant pressure-temperature paths.

At moderate pressures around 38 GPa, Fe_2O_3 remains electronically stable in a HS configuration, even though laser heating up to 2026 K induces transformation from the hematite ($\alpha\text{-Fe}_2\text{O}_3$) structure to the $\text{Rh}_2\text{O}_3(\text{II})$ -type ($\iota\text{-Fe}_2\text{O}_3$) phase. The persistence of a HS signature across this structural transition demonstrates that crystallographic symmetry changes alone do not necessitate an electronic transition, highlighting an early decoupling between structural and electronic degrees of freedom within the HS regime. Thus, at a depth of around 1000 km mainly $\iota\text{-Fe}_2\text{O}_3$ might prevail as an existing phase in HS state.

At intermediate pressures near 64 GPa, Fe_2O_3 enters an extended mixed-spin regime characterized by a step-evolution of the $\text{K}\beta_{1,3}$ XES spectral features and intermediate IAD values ($\zeta\text{-Fe}_2\text{O}_3$). This is due to a sharp one-step HS to LS crossover of iron at specific sites. Laser heating up to 2190 K promotes the formation of mixed-valence iron oxides, dominantly Fe_5O_7 , whose intrinsic coexistence of HS Fe^{2+} and LS Fe^{3+} sites contributes significantly to the observed electronic response. This finding demonstrates that the spin-state inferred from spectroscopic measurements in this pressure regime is governed by the evolving phase assemblage and its coordination. In depths of about 1500 km Fe_2O_3 may not prevail, but instead higher mixed valence oxides like Fe_5O_7 with mixed-spin-states.

At the highest investigated pressure of 80 GPa, all the iron in Fe_2O_3 exhibits a LS state under cold compression ($\theta\text{-Fe}_2\text{O}_3$), consistent with expectations from static compression studies. Upon heating up to 2470 K, however, a pronounced increase in the HS spectral contribution is observed, followed by partial relaxation after quenching. Temperature-quenched XRD reveals that this behavior coincides with extensive phase transformation and the stabilization of $\text{Fe}_{25}\text{O}_{32}$ as the dominant quenched phase. Thus, at depth of about 1800 km, the expected average spin state of the phase assemblage is more in the regime of mixed-spin state with a dominant HS component without main contributions of Fe_2O_3 phases, but instead higher oxides with mixed valences such as $\text{Fe}_{25}\text{O}_{32}$ or possibly $\delta\text{-Fe}_3\text{O}_4$ accompanied by the presence of free oxygen.

Taken together, the results demonstrate that spin crossover in Fe_2O_3 is not a discrete transition tied to a single structural boundary, but a heterogeneous process that unfolds over a broad pressure interval and is strongly modulated by temperature and associated chemical re-equilibration. The emergence of mixed-valence iron oxides at HT introduces additional electronic degrees of freedom that fundamentally alter the spectroscopic signature and must be accounted for when interpreting both laboratory experiments and geophysical models.

From a broader perspective, this work establishes that ferric iron in Fe_2O_3 along the Earth's mantle cannot be described by a single, well-defined spin-state or phase field. Instead, it evolves through coupled electronic, structural, and chemical pathways that depend sensitively on pressure, and temperature. The combined application of XES, RXES, and XRD under *in situ* conditions proves essential for disentangling these effects and provides a robust framework for linking microscopic electronic behavior to macroscopic physical properties.

6 Electronic behavior of haplobasaltic glasses at high pressures depending on Fe^{2+} and Fe^{3+} ratio

6.1 Scientific background

Understanding the behavior of iron in silicate melts at high pressure is central to constraining melt density, partitioning behavior, and the potential formation of long-lived deep mantle reservoirs [6, 18, 19]. The literature on iron behavior in silicate melts and glasses at lower-mantle conditions can be broadly grouped into three, not mutually exclusive, interpretive frameworks: (1) density changes dominated by spin-state modifications of iron [19, 57], (2) gradual structural densification and coordination changes without clearly resolvable discrete electronic transitions [18, 20], and (3) redox- and partitioning-controlled chemical evolution that can occur with or without accompanying spin state changes [14, 15, 22]. The present study is situated at the interface of these frameworks, aiming to disentangle their relative contributions.

Spin-state behavior in HP glasses

A pivotal contribution to the field is the work of Nomura et al. [19], who reported a disappearance of the $\text{K}\beta'$ satellite intensity in Fe^{2+} -bearing silicate glass around 76–77 GPa, interpreted as a spin crossover of Fe^{2+} . This spectral change was correlated with a marked decrease in the Fe-Mg partition coefficient between melt and ferropericlase, leading to the suggestion that spin crossover could promote iron enrichment in deep melts and influence melt density.

Prescher et al. [190] performed SMS on Fe-bearing silicate glasses up to 84 GPa and found no evidence for a sharp HS to LS transition in either Fe^{2+} or Fe^{3+} . Instead, hyperfine parameters evolved continuously with pressure, consistent with gradual densification and coordination changes. The authors argued that any spin transition occurring at mantle temperatures would likely be thermally broadened.

Murakami et al. [191] reported pressure-induced changes in the electronic state of Fe^{2+} in silicate glass, evidenced by the appearance of a new Mössbauer component with lower isomer shift above ~ 20 GPa, which they interpret as the emergence of a mixed-spin-state rather than a complete HS to LS transition. Similarly, Gu et al. [192] observed a gradual decrease in spin moment with increasing pressure in both Al-free and Al-bearing Mg-silicate glasses, reflected in continuous changes in spectral features such as isomer shift and satellite peak intensity. However, their results do not support a sharp HS to LS crossover; instead, they suggest a progressive spin-state evolution to the LS state even at the highest investigated pressures.

Mao et al. on the other hand [193] stated, that when broadening effects of the XES spectra are taken into account, Fe^{2+} and Fe^{3+} in silicate glasses remain in HS state.

Solomatova et al. [194] observed in ferrous iron-bearing glasses over a pressure range up to ~ 120 GPa a continuous coordination evolution of Fe^{2+} and did not observe clear evidence for a spin transition. The observed evolution of hyperfine parameters at HP was interpreted as a structural effect, due to coordination changes, rather than electronic collapse. Importantly, they predict ferrous iron to be in HS state in complex silicate-rich melts in the lower mantle.

Mashino et al. [195] reported HP Mössbauer and electrical-conductivity evidence for pressure-induced changes in the spin/valence environment of iron in peridotite glass (SiO_2 , MgO , FeO , Al_2O_3 , CaO , Cr_2O_3 , Na_2O , NiO , TiO_2 , MnO composition) up to ~ 150 GPa. Above ~ 60 GPa, a new Fe^{2+} component appears and increases in abundance with pressure. The authors interpret this as a progressive HS to mixed-spin-state evolution for Fe^{2+} above ~ 100 GPa. Fe^{3+} remains consistent with HS behavior below ~ 100 GPa, but above ~ 100 GPa its hyperfine parameters suggest a possible HS to LS crossover. The authors further propose that these changes are likely associated with pressure-induced structural compaction of the glass and may contribute to densification of silicate melt analogues at deep-mantle conditions.

These studies highlight that spin-state behavior in silicate glasses at HP remains unresolved, with contrasting interpretations ranging from abrupt spin crossover to gradual, structurally mediated electronic evolution.

Spin-state in melts at simultaneous HP/HT

A major advance beyond room-temperature glass analogues is provided by Shim et al. [57], who directly probed the iron spin-state in a molten silicate under simultaneous extreme pressure and temperature using laser-driven shock compression combined with femtosecond XRD and iron $\text{K}\beta$ XES at an XFEL.

In contrast to static, cold-compressed glass studies that often report gradual changes and/or persistence of HS signatures, Shim et al. [57] observed a strong pressure-dependent reduction in the $\text{K}\beta'$ satellite intensity and associated spectral shifts, consistent with predominantly LS iron in the melt at pressures of ~ 150 - 256 GPa and temperatures of ~ 4000 - 6000 K. Although the dynamic (Hugoniot) compression path and short experimental timescales introduce complexities in interpretation, this study provides the first direct *in situ* constraint on iron spin-state in a true molten silicate at simultaneous HP/HT.

The comparison between static glass experiments and dynamically compressed melts highlights a central question: whether the observed differences arise from temperature effects, timescale effects, or intrinsic differences between glass and melt structures. In particular, Shim et al. propose that structural relaxation in the melt enables stabilization of LS iron at conditions where cold-compressed glasses retain a significant HS population. This tension underscores the need for combined structural and spectroscopic constraints under well-controlled conditions.

Methodological constraints: interpreting Mössbauer parameters

Beyond their descriptive use, the hyperfine parameters derived from Mössbauer spectroscopy are fundamentally linked to the electronic and structural environment of iron. The isomer shift (δ) arises from the electric monopole interaction between the nuclear charge and the *s*-electron density at the nucleus, and reflects the difference in this

electron density between absorber and source. It is therefore sensitive to oxidation state, coordination, and bonding environment. In general, Fe^{2+} exhibits higher isomer shift values than Fe^{3+} , this is due to the inverse proportional increased s -electron density. However, this dependence is not unique, as δ is also influenced by covalency, coordination number, and pressure-induced changes in electronic structure [99].

Quadrupole splitting (ΔE_Q) arises from the interaction between the nuclear quadrupole moment and the electric field gradient at the nucleus. It is therefore highly sensitive to site symmetry and local distortion of the coordination polyhedron. Highly symmetric environments (e.g. regular octahedral coordination) tend to yield small quadrupole splittings, whereas distorted or lower-symmetry environments produce larger values. However, similar ΔE_Q values can result from different combinations of coordination geometry and electronic configuration, further complicating interpretation [99].

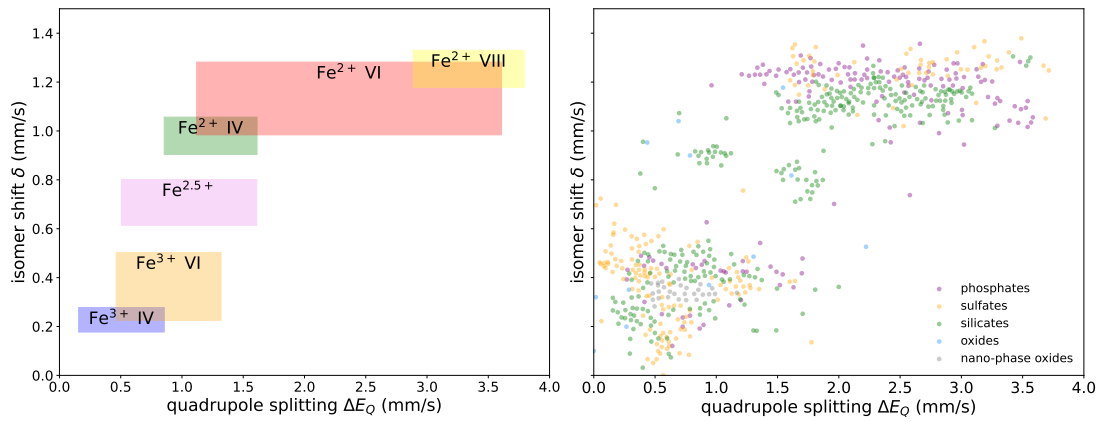


Figure 6.1: Plots of isomer shift (δ) versus quadrupole splitting (ΔE_Q) parameter space for iron in geological materials modified after Dyar and Sklute [99]. **Left)** Schematic fields illustrating typical ranges for Fe oxidation states and coordination environments (digitized with automeris.io from Dyar and Sklute [99]). **Right)** Distribution of experimental data from Dyar and Sklute [99] for different mineral groups (digitized with WebPlotDigitizer [196]), demonstrating substantial scatter and overlap in δ - ΔE_Q space.

As illustrated in Fig. 6.1 (left) after Dyar and Skute [99], the commonly used fields for assigning oxidation state and coordination (e.g. Fe^{2+} vs. Fe^{3+} , tetrahedral vs. octahedral coordination) are presented. The field $\text{Fe}^{2.5+}$ denotes a distinctive feature, representing hyperfine parameters showing a delocalization of electrons (electron hopping) from neighboring Fe^{2+} and Fe^{3+} . Thus, $\text{Fe}^{2.5+}$ shows an averaged value of the isomer splitting. This interaction demonstrates that hyperfine parameters alone do not provide a unique solution for site assignment [99].

The right panel of Fig. 6.1, roughly based on digitized data from Dyar and Sklute, further emphasizes ambiguity by showing the distribution of experimental data for different mineral groups. While general clustering trends are visible (e.g. silicates tending also toward intermediate δ -values and nano-phase oxides extending to lower δ), the scatter within and between groups is substantial. In particular, silicates span a wide range of both δ and ΔE_Q , reflecting the diversity of local coordination environments and bonding configurations in these materials.

These observations highlight a key methodological limitation: Mössbauer hyperfine parameters are not uniquely diagnostic and must be interpreted within a broader context. In complex systems such as silicate glasses and melts, where disorder, mixed coordination, and pressure-induced structural changes are prevalent, multiple configurations may produce similar spectral signatures. Consequently, robust interpretation requires complementary constraints, such as compositional information, structural data (e.g. from XRD or EXAFS) or further spectroscopic measurements on electronic behavior.

In the context of HP studies, additional complications arise from pressure-induced changes in electronic density, coordination number, and spin-state, all of which can affect both δ and ΔE_Q . As a result, trends in hyperfine parameters with pressure must be interpreted cautiously, as they may reflect a combination of electronic, structural, and thermodynamic effects rather than a single, well-defined transition.

Structural densification of melts under compression

Independent of spin-state investigations, structural studies have demonstrated that silicate melts undergo pronounced reorganization under compression. Sanloup et al. [18] provided the first *in situ* structural data on molten basalt up to 60 GPa. Their results show that the silicate network progressively collapses with increasing pressure, accompanied by a continuous increase in silicon coordination from predominantly fourfold toward sixfold, reaching near-octahedral values by ~ 35 GPa. This coordination change is associated with a marked stiffening of the melt and a reduction in compressibility at higher pressures.

At lower pressures, densification is initially dominated by the collapse and reorganization of the tetrahedral network, whereas at higher pressures, compression is increasingly accommodated by bond shortening once higher coordination states are established. These observations highlight that melt densification occurs through multiple structural mechanisms operating over a broad pressure range.

Molecular dynamics simulations (e.g. Bajgain et al. [20]) further support this picture, showing that coordination numbers of all major cations (Si, Al, Fe, Mg, Ca, Na) increase systematically with pressure. The simulations indicate that these changes occur more gradually rather than as abrupt transitions, with most coordination increases taking place below ~ 30 GPa, followed by more continuous structural adjustment at higher pressures. The associated increase in packing efficiency and changes in bonding environment are sufficient to account for the rapid initial densification and subsequent stiffening of basaltic melts.

Together, experimental and computational studies consistently demonstrate that pressure-induced structural evolution (encompassing network collapse, coordination increase, and bond compression) is a primary mechanism controlling the density and compressibility of silicate melts at deep-mantle conditions.

Redox and partitioning controls

Ambient-pressure glass studies [197, 198] demonstrate that $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios can remain constant across varying iron contents even as clustering and coordination environments evolve. Moulton et al. [199] established robust iron K-edge XANES calibrations for $\text{Fe}^{3+}/\Sigma\text{Fe}$ in haplobasaltic glasses, emphasizing the importance of distinguishing redox effects from coordination-driven spectral shifts.

In natural systems, Bézous and Humler [200] showed that MORB mantle sources are relatively homogeneous in oxygen fugacity, whereas Brounce et al. [201] demonstrated elevated $f\text{O}_2$ in arc basalt settings are linked to slab-derived fluids.

Solid-state studies [188, 202–204] demonstrate that spin transitions in ferroperricite and bridgmanite significantly influence mineral’s density, elasticity, and Fe partitioning. Although these works focus on solids, they highlight that electronic transitions can modify thermodynamic properties and element distribution in the deep mantle.

Element partitioning between coexisting phases provides an additional constraint on iron behavior in deep Earth systems. The distribution of iron between minerals and melts depends on its valence state and electronic configuration. In particular, variations in spin-state can influence partitioning behavior by modifying the effective size and electronic structure of the iron cation, which in turn affects its stability in different phases [203]. Consequently, partitioning is linked to the same electronic factors that also influence physical properties such as density and spectroscopic response.

In addition to formal redox equilibria, metal-oxygen charge transfer (MOCT) processes can significantly influence the electronic structure of iron in silicate glasses. These processes involve partial electron delocalization between Fe 3d and O 2p orbitals and are particularly relevant in disordered systems such as glasses.

Spectroscopically, MOCT manifests as broad absorption features in the UV-vis range, including charge transfer bands at high energies, and contributes to shifts in XANES edge positions and pre-edge intensities. For example, optical spectroscopy studies show that absorption features in iron-bearing glasses depend not only on oxidation state but also on coordination environment and glass composition, reflecting changes in Fe-O bonding and electronic structure [205, 206].

Importantly, charge transfer processes can modify spectroscopic observables without requiring a change in formal oxidation state. As a result, variations in spectral features may reflect changes in electron delocalization and bonding environment rather than purely redox-driven transformations, further complicating the interpretation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios derived from spectroscopic measurements [205, 206].

Geophysical context: deep melt stability

Geophysical observations provide independent evidence for the presence of deep partial melt in the lowermost mantle. Yuan and Romanowicz [207] identified large ULVZs beneath plume roots and interpreted them as partially molten regions. Importantly, this interpretation does not require spin crossover as the sole mechanism for seismic velocity reduction.

The existence of deep partial melt is therefore supported independently of the sharp spin-transition hypothesis, but still have an effect if it occurs. However, the physical properties of such melts, including their density and seismic response, depend sensitively on their electronic and structural state. In particular, variations in iron valence, coordination, and electronic configuration may influence melt compressibility, density contrasts, and elastic properties at lower mantle conditions.

The key question is therefore whether melt density and stability at depth are primarily controlled by structural effects, electronic transitions, or a coupled structural-electronic evolution.

Implications for the present study

Across the literature, three key conclusions emerge:

1. Structural densification of silicate melts is well established and begins at moderate lower-mantle pressures.
2. Abrupt spin crossover in melts remains controversial, with increasing evidence supporting a gradual electronic evolution.
3. Redox and partitioning effects alone are insufficient to explain the full range of observed melt density variations, requiring consideration of both structural and electronic contributions.

The present study directly addresses the unresolved interplay between these mechanisms. By constraining iron spin-state and coordination behavior under high pressure, it contributes to determining whether deep mantle melt stability is primarily controlled by structural effects, electronic transitions, or their coupled evolution.

Resolving this issue is essential for interpreting dense melt formation, the stability of a basal magma ocean, and the origin of deep mantle heterogeneities.

6.2 Structure and properties of haplobasaltic glasses

Glass

A glass is a non-crystalline (amorphous) solid that forms when a liquid is quenched without crystallizing, so that long-range periodic atomic order does not develop. Unlike crystalline solids, which exhibit translational symmetry and long-range periodicity, glasses lack long-range periodicity but still show well-defined short-range order (SRO) and often intermediate-range order (IRO) over nanometer length scales [208].

From a thermodynamic theoretical perspective, glass is metastable relative to crystalline phases of the same composition (where such crystalline phases are accessible), because the glass structure is arrested before it can reach the crystalline equilibrium state [209]. The glass transition is not a simple phase transition. Rather, it is a phenomenon in which the structural relaxation time of the cooled liquid becomes longer than the experimental timescale, causing the system to fall out of equilibrium into an amorphous solid [209]. Consequently, the atomic configuration of a glass can be cautiously viewed as a frozen-in liquid structure that can reflect the structure of the melt at (or near) quench conditions [3, 22, 208].

For silicate compositions, this frozen-in character motivates the common use of silicate glasses as structural analogues for melts, particularly in high-pressure studies where *in situ* characterization of molten structure is experimentally challenging [18, 22, 208] (cf. 2.5).

Structure of silicate glasses compared to crystals

The fundamental structural unit in most silicate materials is the SiO_4 tetrahedron (and related tetrahedrally coordinated network-forming units) at low pressures [3, 208]. In crystalline silicates, these tetrahedra are arranged in periodic networks (chains, sheets, or frameworks) with bond lengths and angles constrained by crystallographic symmetry

and discrete lattice sites, whereas in silicate glasses the same local tetrahedral units are preserved but are connected in a disordered, no-periodic network.

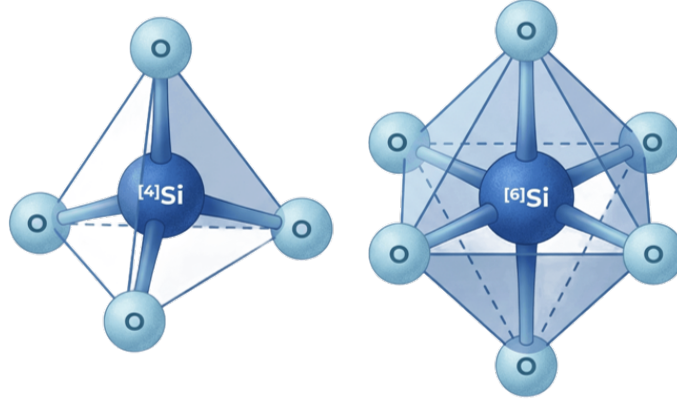


Figure 6.2: Schematic of **left**) SiO_4 tetrahedron at low pressure and **right**) SiO_6 octahedron at high pressure. Improved with AI [35].

In contrast, silicate glasses consist of a disordered network of tetrahedra linked by shared oxygen atoms (bridging oxygens, BO), forming a continuous random network without periodicity [3]. Network connectivity is commonly described using Q^n species, where n denotes the number of BO per tetrahedron [3]. Fully polymerized networks (e.g. SiO_2 glass) are dominated by Q^4 units, whereas more depolymerized compositions (including basaltic systems) have higher fractions of lower n (Q^2 - Q^3) associated with increased NBO abundance [3, 210].

In depolymerized silicate melts and glasses, network-modifying cations (e.g. Ca^{2+} , Mg^{2+} , and commonly Fe^{2+}) contribute to charge-balancing and promote NBO formation, thereby reducing average network connectivity [3, 208].

Compared to crystals, glasses typically exhibit broad distributions of bond angles and local geometries rather than discrete crystallographic values, and they exhibit distributions of local environments rather than a small number of symmetry-equivalent sites [3, 208].

Under compression, silicate glasses and melts undergo progressive structural densification that includes changes in coordination environments and network topology [18, 208]. In basaltic liquids, both experiment and first-principles simulations show that mean Si-O coordination increases with pressure from values near fourfold at low pressure toward higher coordination (sixfold becoming increasingly abundant) over tens of GPa [18, 20]. In liquids and glasses this evolution is typically more gradual rather than occurring as a sequence of sharp polymorphic transitions characteristic of crystals [20].

Haplobasaltic glass structural characteristics

HBGs represent simplified basaltic compositions designed to isolate key controls on basaltic melt structure while keeping experiments tractable [18, 199]. Such simplified basaltic systems are widely used as analogues for natural basaltic melts in structural and spectroscopic studies [18, 20].

Basaltic (and haplobasaltic) networks are generally moderately depolymerized relative to silica-rich compositions, with appreciable NBO populations and mixed Q^n distributions. Because glasses preserve melt-like SRO, they can be used as structural analogues for investigating melt structure. In particular, spectroscopic techniques such as XANES, XES, and Mössbauer spectroscopy provide access to cation coordination environments, including Fe coordination and their evolution with pressure [99, 199].

However, glasses represent kinetically arrested, room-temperature structures and do not reproduce the dynamical rearrangements (diffusion, continuous bond exchange, and time-dependent relaxation) present in melts [22, 208]. Accordingly, extrapolating from quenched glasses to melts requires care, particularly when temperature, timescale, or relaxation effects are expected to modify structural populations or spectroscopic observables [22, 57]. Further elaboration can be found in 2.5.

Iron in silicate glasses: structural role

Iron in silicate glasses and melts occurs predominantly as Fe^{2+} and Fe^{3+} , and the relative proportions depend on bulk composition, temperature, pressure, and oxygen fugacity during equilibration of the melt [210]. The Fe^{3+}/Fe_{tot} ratio in natural magmatic liquids can vary over nearly the full range from 0 to 1 and is widely used as an indicator of oxygen fugacity and redox conditions [210].

Fe^{3+}

Although Fe^{3+} and Al^{3+} share the same nominal charge, they do not necessarily occupy identical structural environments. Whereas Al^{3+} is dominantly tetrahedrally coordinated in silicate systems, Fe^{3+} commonly exhibits sixfold coordination in crystalline silicates, though exceptions exist [210].

In silicate glasses, the oxygen coordination number of Fe^{3+} varies with bulk composition and total iron content. Both tetrahedral and higher coordination environments have been documented, and multiple coordination states may coexist in chemically complex systems [210]. The Fe^{3+} -O bond distance is commonly used as an indicator of coordination number, with increasing bond length consistent with increasing coordination [210].

The structural role of Fe^{3+} depends strongly on its coordination environment. Tetrahedrally coordinated Fe^{3+} commonly acts as a network former by participating directly in the silicate framework through FeO_4 units and Fe-O-Si linkages. In contrast, higher coordinated Fe^{3+} species, particularly fivefold and sixfold coordinated Fe^{3+} , are generally considered intermediate or network-modifying species that contribute less directly to network polymerization [21, 81].

Fe^{2+}

Ferrous iron typically occupies higher coordination environments than Fe^{3+} in silicate systems. In FeO-SiO₂ compositions, Fe^{2+} -O bond distances are commonly consistent with predominantly sixfold coordination, although some data suggest coordination numbers between 4 and 6 depending on composition [210].

In contrast to tetrahedrally coordinated Fe^{3+} , Fe^{2+} is generally regarded as a network modifier in silicate glasses. Owing to its predominantly higher coordination environment, Fe^{2+} tends to disrupt Si-O-Si linkages and promote the formation of NBOs, thereby depolymerizing the silicate network [21].

Structure-density relation

The structural role of iron influences melt and glass density because the partial molar volumes of FeO and $\text{FeO}_{1.5}$ depend on oxygen coordination [210]. The partial molar volume of FeO in glass ($\approx 13\text{-}14\text{ cm}^3/\text{mol}$) is comparable to that of crystalline FeO , indicating sixfold-coordinated Fe^{2+} . In contrast, the partial molar volume associated with Fe^{3+} varies with coordination state, reflecting differences between tetrahedral and octahedral coordination [210].

Because the partial molar volumes of iron oxides depend on oxygen coordination [210], and silicate melts densify under pressure through progressive increases in coordination [18, 20], pressure-induced changes in Fe coordination may contribute to densification independently of spin-state transitions. Structural and electronic effects should therefore be evaluated separately when interpreting density evolution in haplobasaltic glasses at high pressure.

Relevance for high-pressure studies

In lower-mantle relevant research, haplobasaltic glasses provide experimentally tractable analogues for basaltic melts and allow controlled investigation of pressure-driven coordination changes and their coupling to iron electronic behavior using complementary spectroscopies [18, 20, 199]. Establishing the baseline structural response of amorphous silicate networks to compression is essential for interpreting high-pressure spectroscopic changes, and for assessing how network topology, iron valence, coordination environment, and possible spin-state evolution jointly influence melt/glass density and stability in deep planetary interiors [18, 20].

6.3 Data extraction, processing, energy calibration, challenges

The following section explain data handling regarding two experiments at ID20 for XES measurements and one experiment at ID18 (now ID14) for SMS measurements, which were performed parallel with the first ID20 experiment.

6.3.1 Synchrotron Mössbauer spectroscopy

The measured SMS data at ID18 was calibrated on site and saved. For further analysis SYNCmoss [211] was used for the fitting process. The model files exported from SYNCmoss (cf. Fig. 6.3) contain the fitted spectral components and their parameters and were reprocessed in Python to reconstruct the spectra using the same approach and instrumental response functions. The model consists of two sample doublets (Fe^{2+} and Fe^{3+}) and one fixed doublet representing the beryllium (Be)-lens contribution.

Asymmetric doublets were used because of possible overlap of isomer shift δ and quadrupole splitting ΔE_Q in glasses. Further, one doublet for Fe^{2+} and Fe^{3+} was chosen, since the data was reproduced well and the χ^2 is in the range between 0.52 and 1.38 for all spectra.

The measured spectra, recorded as count rates as a function of Doppler velocity v , were converted to relative transmission by normalizing to an estimated baseline intensity N_0 , yielding $T(v) = N(v)/N_0$. The reconstructed model, which has an arbitrary numerical

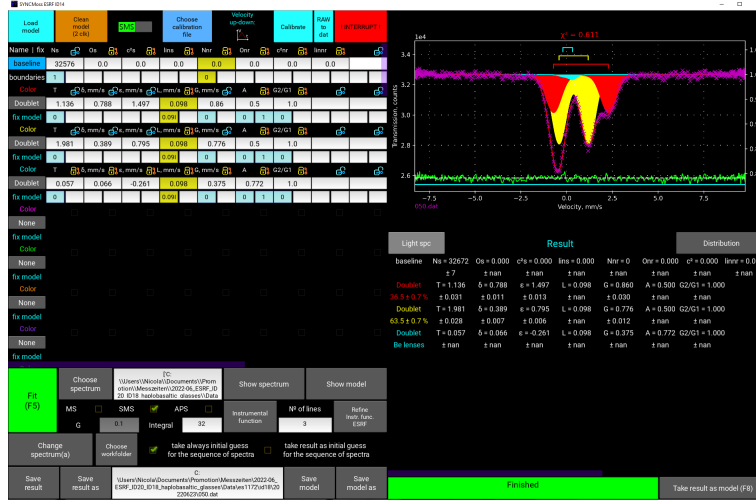


Figure 6.3: Screenshot of an example spectrum and model in SYNCmoss [211], showing the GUI and its variety of features.

scaling, was linearly transformed to match the measured transmission spectrum according to $T_{\text{fit}}(v) = A F_{\text{raw}}(v) + B$. Residuals were calculated as $T_{\text{data}}(v) - T_{\text{fit}}(v)$.

For visualization, the total spectrum was decomposed into contributions from the individual doublets, allowing the relative contributions of Fe^{2+} , Fe^{3+} , and the Be-lens signal to be compared on a common baseline.

The fitted hyperfine parameters (intensity I , isomer shift δ , and quadrupole splitting ΔE_Q) were extracted from the model parameters. The center shift is treated as the isomer shift, assuming a constant Doppler contribution under comparable experimental conditions.

The Fe^{2+} and Fe^{3+} doublets were assigned based on their isomer shifts, with higher δ corresponding to Fe^{2+} . Their intensities were used to calculate

$$\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} = \frac{I_{\text{Fe}^{2+}}}{I_{\text{Fe}^{3+}}} \quad (6.1)$$

and

$$\frac{\text{Fe}^{3+}}{\text{Fe}_{\text{tot}}} = \frac{I_{\text{Fe}^{3+}}}{I_{\text{Fe}^{2+}} + I_{\text{Fe}^{3+}}}. \quad (6.2)$$

These quantities were evaluated as a function of pressure for all glass compositions.

6.3.2 X-ray emission spectroscopy

Iron $\text{K}\beta$ X-ray emission spectra of haplobasaltic glasses were collected using a von Hámos spectrometer at ESRF ID20 (cf. Sahle et al. [150]). The detector records a two-dimensional image (cf. Fig. 6.4) in which the emitted photon energy is encoded spatially along the dispersive direction. Data reduction therefore consists of transforming 2D detector images into calibrated 1D spectra through definition of ROIs, energy calibration (pixel-to-energy mapping), accumulation of scan sequences, background subtraction and

spectral interpolation onto a common energy grid. All steps were implemented using IXStools [212] in combination with custom spectrum-processing python script.

Conceptual distinction from Fe_2O_3 experiments

The calibration strategy differs fundamentally from that used in the Fe_2O_3 study, which was performed at P01. In the Fe_2O_3 experiments, the incident energy was scanned while the spectrometer geometry remained fixed. The elastic line moved across the detector, enabling a direct pixel-to-energy mapping from the known incident energy.

In contrast, for the haplobasaltic glass measurements, the elastic scattering was recorded by varying both the incident energy and the spectrometer geometry (detector/analyzer arm). Accordingly, the elastic peak was observed at different detector positions due to the combined effect of incident-energy variation and mechanical scanning of the spectrometer.

This distinction is critical, the pixel-to-energy mapping is obtained from the elastic peak positions generated during the combined scan of incident energy and spectrometer geometry, rather than from geometry alone.

Implementation in the analysis code

The energy calibration was performed independently for each analyzer crystal (two for the first experiment and three for the second experiment). For each crystal, a ROI corresponding to the analyzer footprint on the detector was defined and applied to dedicated calibration scans. These consisted of an elastic scattering scan and a detector-position scan recorded while the spectrometer geometry was varied.

From these scans, the trajectory of the elastic line across the detector was determined. Because the energy of the elastic line is equal to the incident photon energy, each observed detector position of the elastic peak corresponds to a known photon energy. This information was used to establish a relation between detector pixel position and emitted photon energy.

The calibration procedure therefore determines the pixel-to-energy mapping

$$E = f(p), \quad (6.3)$$

where p denotes the detector pixel coordinate within the ROI and E the emitted photon energy. The resulting dispersion relation was stored and subsequently applied to all emission spectra recorded under identical spectrometer settings. Two calibration scans are required:

- **Elastic scan** A scan recorded at fixed incident energy in which the elastic line is measured while the spectrometer geometry is varied. The elastic peak therefore appears at different detector positions.
- **Detector-position scan** A scan providing the corresponding mechanical position (e.g. analyzer angle or detector translation) for each image.

For each detector image in the elastic scan, the ROI is applied, and the 2D intensity distribution is reduced to a 1D projection along the dispersive direction. Afterwards, the centroid (or maximum) position p_i of the elastic peak is determined. The corresponding mechanical spectrometer coordinate x_i is obtained from the detector-position scan. Because the elastic scattering energy equals the incident photon energy E_0 , each centroid position p_i corresponds to a known photon energy E_0 . The mechanical coordinate x_i and

detector pixel p_i are related through the spectrometer geometry. Using Bragg's law the analyzer angle Θ (derived from x_i) determines the photon energy. The calibration routine therefore establishes a correspondence between detector pixel positions p_i and photon energies E_i . A polynomial (or spline) fit is then used to construct a smooth dispersion relation $E = f(p)$ valid over the entire ROI range. Because the calibration depends only on spectrometer geometry and crystal alignment, it remains valid for all scans acquired under identical instrument settings and fixed sample position. The calibration is therefore performed once and stored as an HDF5 axis file, which is subsequently loaded during routine data reduction.

ROI definition and detector masking

Individual ROIs were defined and stored separately for each analyzer crystal. This approach ensures that only spectra with identical spectral shape are combined during subsequent processing. By enforcing consistent ROI boundaries, variations in spectral shape arising from differing crystal alignments or detector positions are avoided. If a given crystal does not provide a spectrum fully compatible with the others, its contribution is excluded from further analysis.

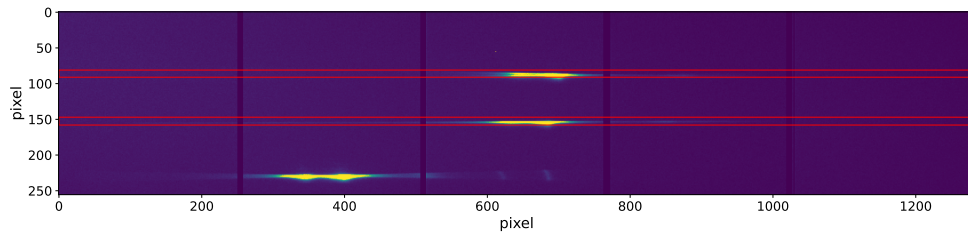


Figure 6.4: Detector image including the exemplary ROI area marked in red including the $K\beta$ emission signal in yellow. The vertical detector panels are visible by separating black lines. The emission spectra on the bottom originates from $K\alpha$ emission.

A detector mask was constructed to exclude inactive vertical stripes between detector panels. Pixels in these regions were identified and incorporated into each ROI as a filter image. In this way, defective or inactive pixels were systematically excluded from the spectral extraction.

A detector image including exemplary ROIs around the two $K\beta$ emission signals with a height of 10 pixels is shown in Fig. 6.4. For clarification purposes: crystal 3 in the first experiment was showing $K\alpha$ emission and during the second experiment, it was not focused enough for the $K\beta$ emission. Therefore, crystal 3 is not used in the following analysis.

Spectrum extraction, accumulation, background subtraction

For each pressure point, several scans were recorded, each consisting of multiple detector images. These scans were grouped and accumulated in order to improve counting statistics. For the spectrum extraction, the scans were loaded, together with the region of interest corresponding to the respective analyzer crystal. Using the previously determined energy calibration, the detector pixels within the ROI were converted to

photon energy. After background correction, each spectrum was restricted to 7000-7140 eV, normalized, and interpolated onto a common grid. This procedure yields the raw emission spectrum $I_{\text{raw}}(E)$ for each analyzer crystal.

The background was estimated by vertically shifting the ROI by ± 20 pixels and repeating the extraction. This samples detector background and diffuse scattering adjacent to the emission line. For the first crystals' signal the background spectrum $I_{\text{bgr}}(E)$ was scaled by a factor a :

$$a = \frac{\langle I_{\text{raw}}(E) \rangle_{[E_1, E_2]}}{\langle I_{\text{bgr}}(E) \rangle_{[E_1, E_2]}} \quad (6.4)$$

in a background-dominated energy interval, and subtracted: $I(E) = I_{\text{raw}}(E) - a I_{\text{bgr}}(E)$. In addition to this, a low-order polynomial baseline correction was applied to the emission signal of the second analyzer crystal, because of a residual background.

6.3.2.1 Challenges

During analysis, several complications were identified.

(i) Analyzer crystals

The two analyzer crystals exhibited significantly different spectral shapes (cf. Fig. 6.5). These differences may arise from variations in focussing or crystal imperfections. As a result, spectra from crystal 1 and crystal 2 could not be reliably summed. An example is shown in Fig. 6.24. All analysis was therefore performed on each crystal independently.

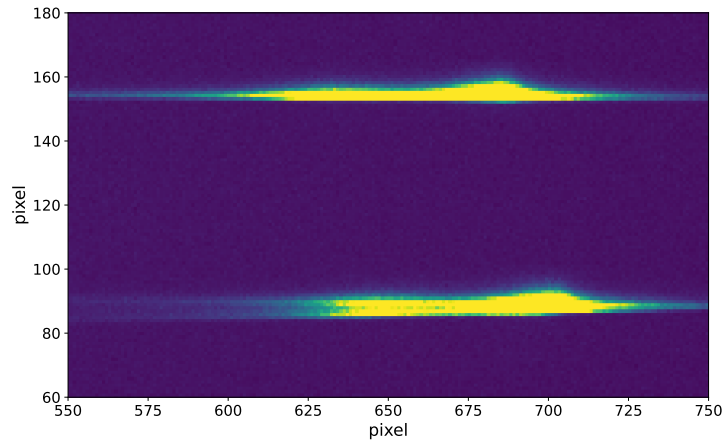


Figure 6.5: Detector image with zoom onto the $\text{K}\beta_{1,3}$ emission region. A discrepancy between the two crystals is noticeable and hinder a summation of both crystals for further analysis.

(ii) Panel gap crossing the spectrum

The 2D detector consists of multiple panels separated by inactive regions. A pronounced intensity dip occurs at panel boundaries. Throughout the measurement of a single scan, and thus certain spectrometer geometries, the Fe $\text{K}\beta$ emission line crossed such a

boundary. In these cases, the dip artificially distorted the spectral profile and produced intensity minima.

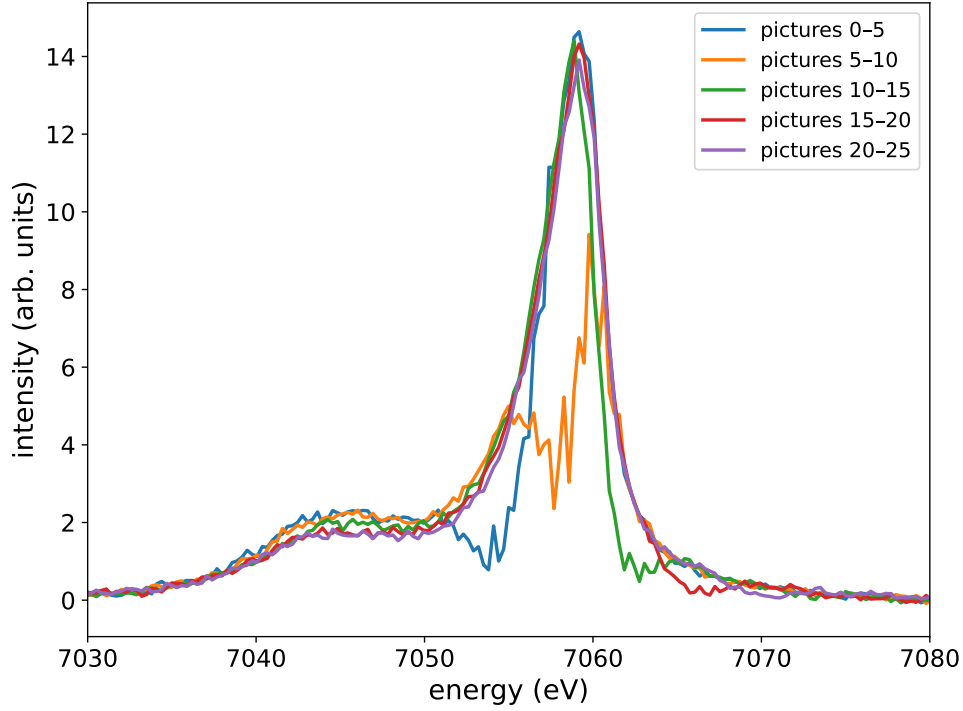


Figure 6.6: XES $K\beta$ emission spectra from a single scan, grouped in intervals of five images of the affected pictures. The figure illustrates the change in spectral shape before, during, and after crossing a detector panel boundary, as well as spectra directly affected by the panel gap.

Figure 6.6 demonstrates the effect of the panel gap crossing on the spectral shape before, during, and after the crossing event in the first experiment. Notably, images 25 to 40 (out of 40 images per scan) were consistently recorded on the same detector panel and exhibit a stable spectral shape.

For the second experiment, images 0 to 40 (out of 120 images per scan) were recorded on the same panel and show a stable spectral shape.

In principle, intensity variations introduced by panel gaps could average out during summation. However, in the present case this compensation does not occur due to the additional effects discussed in the following point (iii).

(iii) Panel-dependent sensitivity

For investigating the detector panels' sensitivity, ROIs were set around the emission, to detect the background scattering, which is expected to change continuously, as shown in Fig. 6.7) and integrated.

Fig. 6.8, with the integrated background from the ROIs, clearly shows a distinct offset between each detector panel because of different sensitivities of each panel.

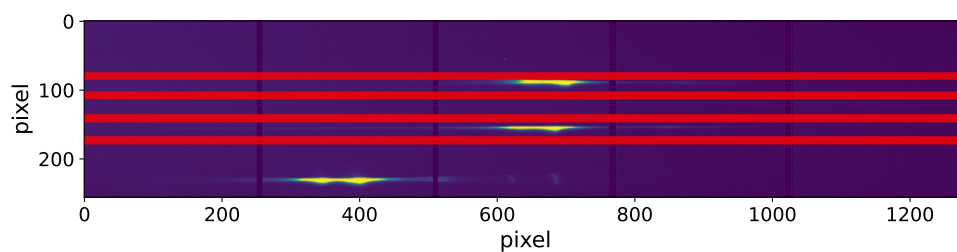


Figure 6.7: Detector image with 4 different ROIS around the emission signal.

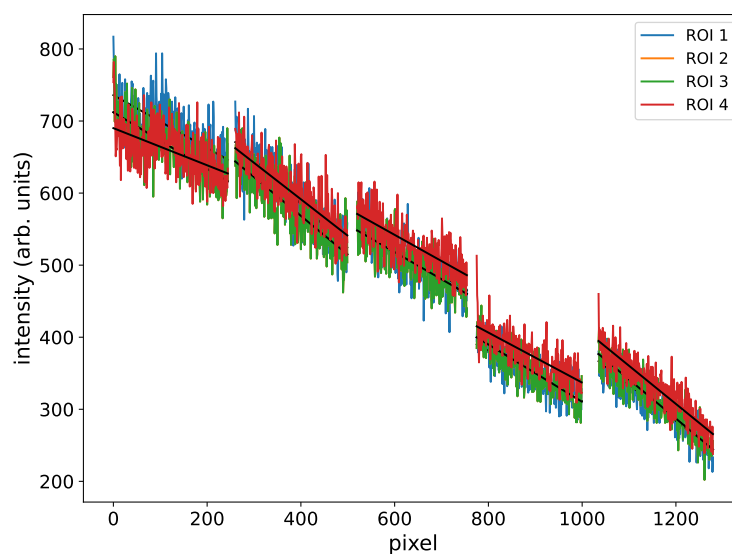


Figure 6.8: Integrated background signal from each panel per ROI with a linear fit in black showing also different slopes beside the intensity offset. The gaps between spectra are the detector panel gaps, which would be set to zero, but are here not taken into account.

In order to avoid systematic error from scaling between the discontinuity, this method was not applied. This leads to systematic distortions in peak ratios and spectral shape and needs to be minded, when analyzing the XES spectra.

Data rejection criterion

To ensure credibility, all scans in which the entire emission spectrum was not fully contained within a single detector panel were discarded. Only geometries where the complete $K\beta$ feature lay on one continuous detector panel were retained for quantitative analysis. This selection criterion was essential to avoid artifacts from panel gaps and sensitivity mismatches. As a consequence, the data quality is reduced. Moreover, each crystals' signal will be analyzed separately.

6.3.2.2 First moment analysis of the $K\beta_{1,3}$ emission line

To quantify the spin-state evolution of iron in the HBGs, the first moment (M1) of the Fe $K\beta$ emission line was determined. M1 describes the center of mass of the spectral intensity distribution and provides a robust measure of the spectral shift associated with spin state changes in iron. Previous studies have demonstrated that the $K\beta$ emission line shape and position are sensitive to the number of unpaired $3d$ electrons through the $3p$ - $3d$ exchange interaction, making M1 a suitable proxy for the spin-state [28, 161].

For each spectrum, the energy interval used for calculating the M1 was determined from the half-maximum of the main emission line, as shown in Fig. 6.9, where the CMS is calculated within this energy interval.

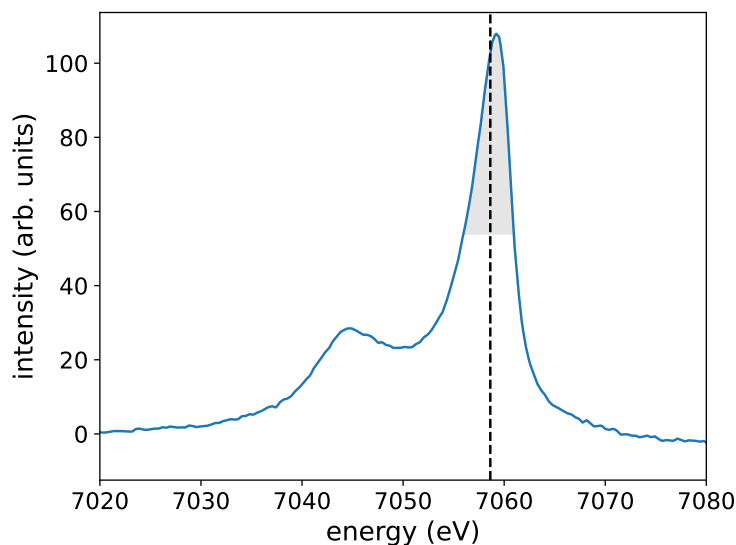


Figure 6.9: $K\beta$ emission spectrum of iron in HS state with the used area marked in grey for CMS determination for the M1 analysis and the black dashed line indicates the calculated M1 energy position.

For each experimental spectrum, the half-maximum positions were determined and the M1 was calculated using the same procedure as for the reference spectra.

In addition to the M1 approach, the IAD method was tested for spin-state determination. However, this method did not yield reliable results for the present dataset.

The IAD technique requires careful alignment and normalization of all spectra relative to a reference spectrum before the integrated absolute difference can be evaluated. In the present case, this procedure was hindered by variations in spectral shape.

As the IAD method is particularly sensitive to such spectral distortions, the resulting values exhibited substantial scatter and did not define a consistent pressure-dependent trend. Therefore, the M1 analysis was used as the primary approach for quantifying spin-state variations and was proven as robust in a previous study from Albers et al. [161].

6.4 Experimental results

Two experimental sessions were conducted. During both sessions, XES measurements were performed using the von Hámos spectrometer at beamline ID20. In addition, SMS measurements were carried out in parallel during the first experiment at beamline ID18. During the second session additional XANES characterization on ambient samples was performed at ID24.

HBG samples with three different iron oxidation states (61%, 47%, and 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$, cf. Sec. 4.2) were investigated at pressures up to 120 GPa. In addition, Fe^{2+} and Fe^{3+} reference compounds were measured for comparison. In the following, the terms Glass and HBG (1-3) are used interchangeably, where HBG 1 denotes the sample with the highest $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio (61%), HBG 2 a content of 47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ and HBG 3 the lowest (13%).

6.4.1 X-ray absorption near-edge spectroscopy characterization

XANES characterization measurements were performed by Prof. Dr. Max Wilke at beamline ID24 at the ESRF during the second experiment. The spectra of the HBG samples and the reference materials at ambient pressure are shown in Fig. 6.10. The spectra display a systematic shift of the absorption edge and pre-peak position with increasing Fe^{3+} content. Samples with higher Fe^{3+} contents exhibit higher centroid energies, whereas Fe^{2+} -rich samples show lower values. Two regimes can be distinguished based on the pre-peak position: a lower-energy group consisting of the Fe^{2+} reference and HBG 3, and a higher-energy group comprising the Fe^{3+} reference together with HBG 1 and HBG 2.

The shift of the XANES centroid position towards higher energies reflects an increase in the average Fe oxidation state. This behavior arises from the higher effective nuclear charge experienced by the absorbing atom in Fe^{3+} compared to Fe^{2+} , and also increases the onset energy of the absorption edge.

The $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio can be estimated from the centroid position of the XANES spectra following the method of Wilke et al. [84] (Tab. 6.1). The measurements and calculations were performed by Prof. Dr. Max Wilke.

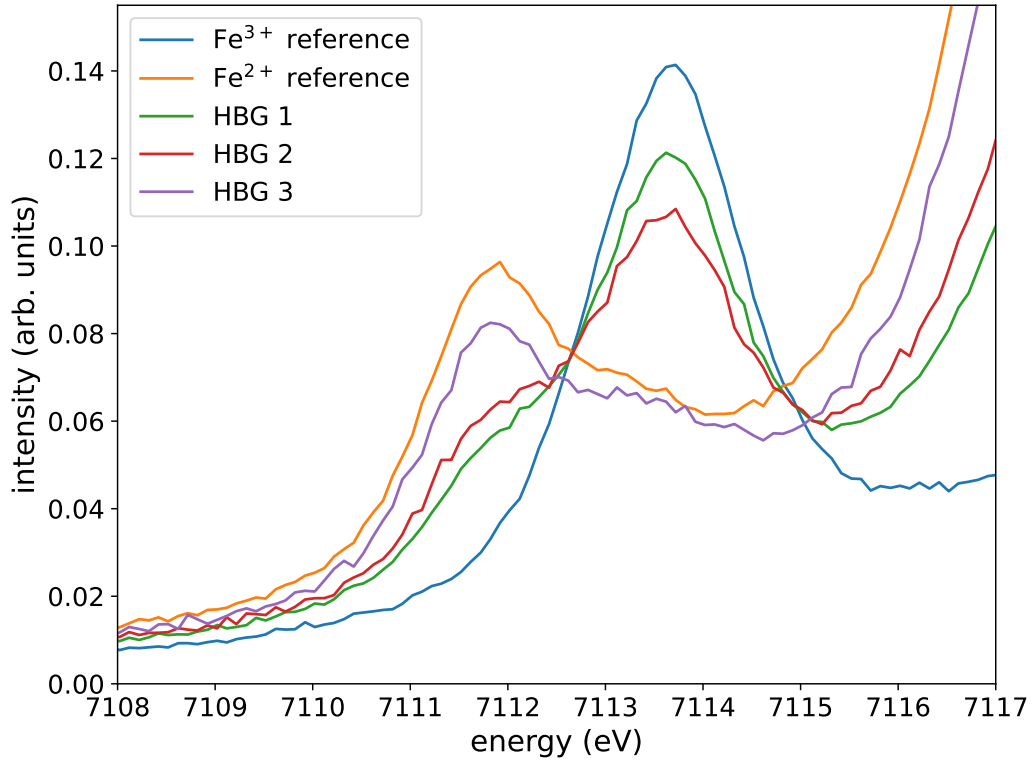


Figure 6.10: XANES spectra of Fe^{2+} and Fe^{3+} reference compounds together with three HBG samples containing 61%, 47%, and 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$.

Table 6.1: Centroid energies and calculated and rounded $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios for reference compounds and HBG glasses. For context the WCCA results for HBG 1-3 are added.

sample	centroid (eV)	$\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$	WCCA
Fe^{3+}	7113.58	> 100	-
Fe^{2+}	7112.05	2	-
HBG 1 (61%)	7113.21	59	61
HBG 2 (47%)	7113.04	48	47
HBG 3 (13%)	7112.26	10	13

The $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios previously derived from WCCA (cf. Tab. 4.2) are retained as reference values because they were determined using well-established calibration procedures and multiple analytical points per sample. Nevertheless, the ratios calculated from the XANES centroid positions show very good agreement with the WCCA results.

For HBG 1, the deviation between the XANES-derived and WCCA-derived $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios is 2%. HBG 2 shows an even smaller deviation of 1%. HBG 3, which has the lowest $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio, exhibits a slightly larger deviation of 3%.

Overall, the XANES-derived $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios are in very good agreement with the WCCA values, with deviations of maximum 3%. This consistency confirms that the investigated glasses cover a broad and well-constrained redox range. The samples therefore provide suitable starting compositions for investigating the pressure-dependent evolution of the Fe electronic and magnetic state in haplobasaltic glasses.

6.4.2 Synchrotron Mössbauer spectroscopy results

In the following, results from SMS measurements on the three HBG glasses are presented. First, representative spectra and their fits are shown, followed by the pressure dependence of hyperfine parameters and ferric iron fraction ($\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$).

6.4.2.1 Representative spectra

The SMS spectra were fitted using a model consisting of two doublets assigned to Fe^{2+} and Fe^{3+} , together with a third doublet originating from the Be-lens. The Be-lens contribution was kept fixed during fitting. Spectra are shown for ambient conditions as well as for selected pressures within the DAC. Because a total of 32 spectra were collected, only representative spectra at the lowest and highest pressures are shown here; the full dataset is provided in Appendix A.8.1.

Ambient samples

Representative ambient-pressure SMS spectra of the three HBGs are shown in Figures 6.11–6.13. The measurements were performed outside the DAC (see Appendix Fig. A.33 b)).

The measured transmission spectra (black crosses) are well reproduced by the fitted model (black line), and the residuals show no systematic deviations, indicating that the adopted three-doublet model adequately describes the data. The relative areas of the Fe^{2+} and Fe^{3+} doublets reflect the ferric/ferrous iron fraction of the samples. It should be noted that the ambient spectra were measured outside the DAC on irregular glass fragments with variable thicknesses and sizes, rather than on polished or thickness-optimized absorbers (cf. Fig. A.33 (b)).

The ambient-pressure SMS spectra of the three HBG glasses display clear differences in the relative contributions of the Fe^{2+} and Fe^{3+} doublets, reflecting the distinct initial ferric iron fractions of the samples. In all spectra, the characteristic doublet structure typical for paramagnetic Fe-bearing glasses is observed, consisting of two absorption minima asymmetrically distributed around zero velocity. These features arise from

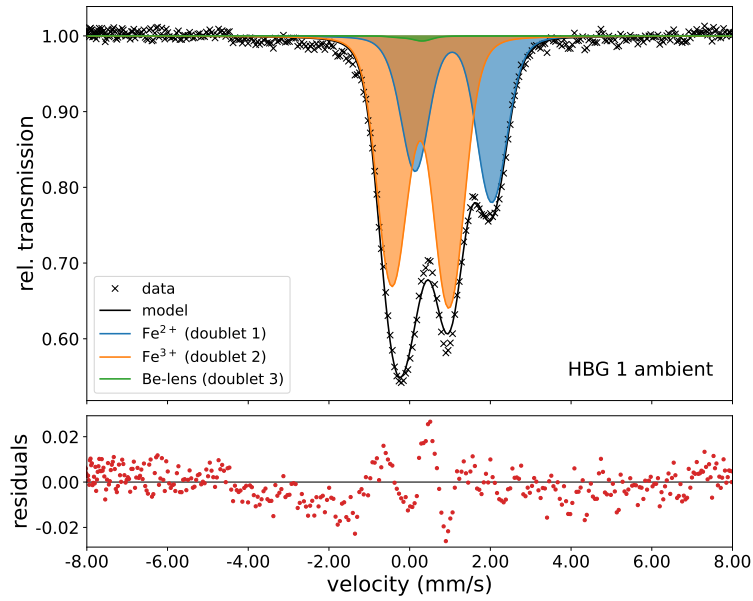


Figure 6.11: Ambient-pressure SMS spectrum of HBG 1 with an initial ferric iron fraction of 61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. Black crosses represent the measured data and the black line shows the fitted model. The individual spectral components corresponding to Fe^{2+} (doublet 1), Fe^{3+} (doublet 2), and the Be-lens contribution (doublet 3) are indicated by colored areas. Residuals of the fit are shown in the lower panel.

quadrupole splitting of the nuclear energy levels and correspond to Fe in different oxidation states and local coordination environments within the glass structure.

In HBG 1 (Fig. 6.11), which has the highest initial ferric iron fraction (61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$), the spectrum is dominated by the Fe^{3+} doublet. This component produces the most pronounced absorption features and contributes the largest fraction to the overall spectral area. The Fe^{2+} doublet is present but contributes less strongly to the overall spectral shape. Consequently, the absorption minima associated with Fe^{3+} are more prominent, consistent with the relatively oxidized character of this glass.

In contrast, the ambient spectrum of HBG 3 (13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) (Fig. 6.12) is dominated by the Fe^{2+} doublet. The Fe^{2+} contribution produces the strongest absorption features, whereas the Fe^{3+} doublet appears only as a smaller component on the spectrum. This behavior reflects the more reduced character of this glass composition, in which the majority of iron is present as Fe^{2+} .

The spectrum of HBG 2 (47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) (Fig. 6.13) exhibits intermediate characteristics of the HBG samples. In this case, the Fe^{2+} and Fe^{3+} doublets contribute comparable spectral areas, resulting in a spectrum in which both components significantly influence the overall line shape. The relative intensities of the two doublets therefore closely reflect the intermediate ferric iron fraction of this sample. Overall, the systematic variation in the relative contributions of the Fe^{2+} and Fe^{3+} doublets among the three glasses is consistent with their independently determined bulk $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios and confirms that the fitted spectral components reliably capture the redox state of iron in the glasses at ambient conditions.

In all spectra, the additional doublet originating from the Be lens is visible as a small

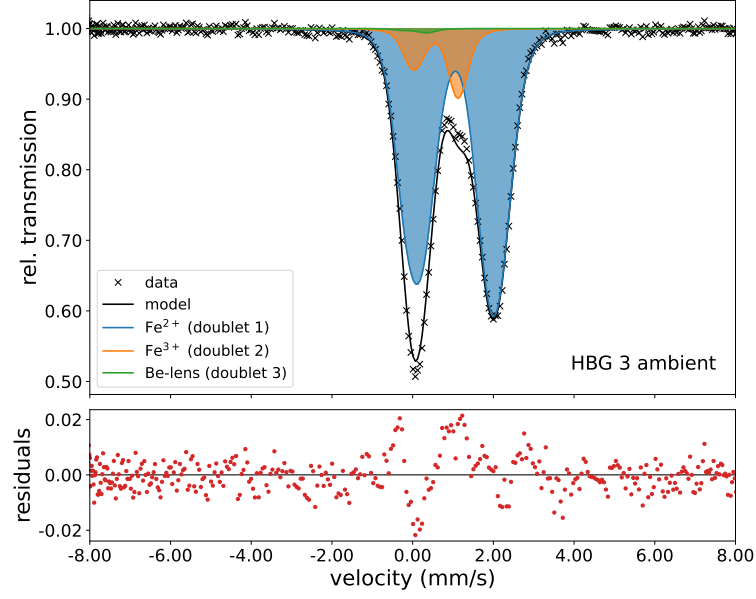


Figure 6.12: Ambient-pressure SMS spectrum of HBG 3 with an initial ferric iron fraction of 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. Symbols, model curve, and color-coded spectral components correspond to those described in Figure 6.11. Residuals of the fit are displayed in the lower panel.

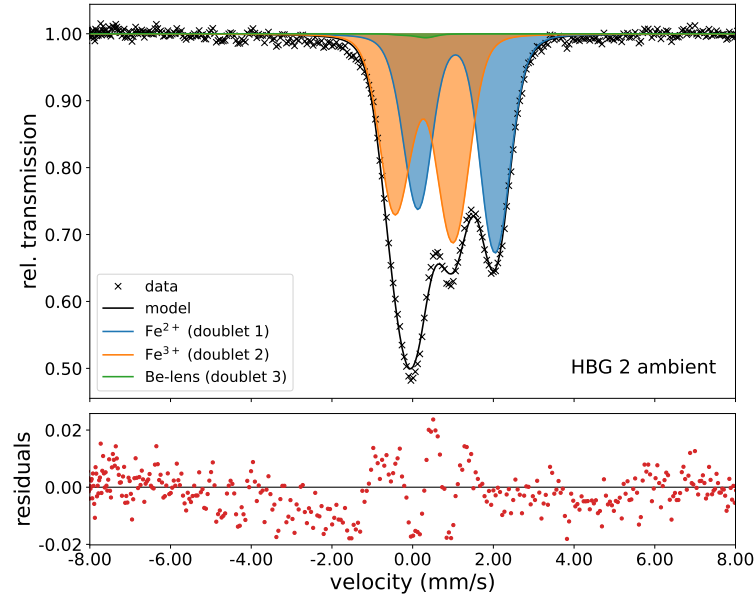


Figure 6.13: Ambient-pressure SMS spectrum of HBG 2 with an initial ferric iron fraction of 47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. Symbols, model curve, and color-coded spectral components correspond to those described in Figure 6.11. Residuals are shown in the lower panel.

and symmetric contribution centered near zero velocity. Because this component arises from the experimental setup rather than the sample itself, it was included as a fixed contribution during the fitting procedure and was not considered in the determination of the ferric iron fraction. The good agreement between the measured spectra and the fitted models, as well as the randomly distributed residuals, indicate that the three-doublet model provides an adequate description of the experimental data.

HBG 1 61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$

The SMS spectra of HBG 1 measured at 38 GPa and 100 GPa are shown in Fig. 6.14. In both spectra the characteristic doublet structure typical for paramagnetic Fe-bearing glasses is preserved, consisting of two pairs of absorption minima distributed around zero velocity. Alas, a slight difference to the ambient sample quadrupole splitting is observable.

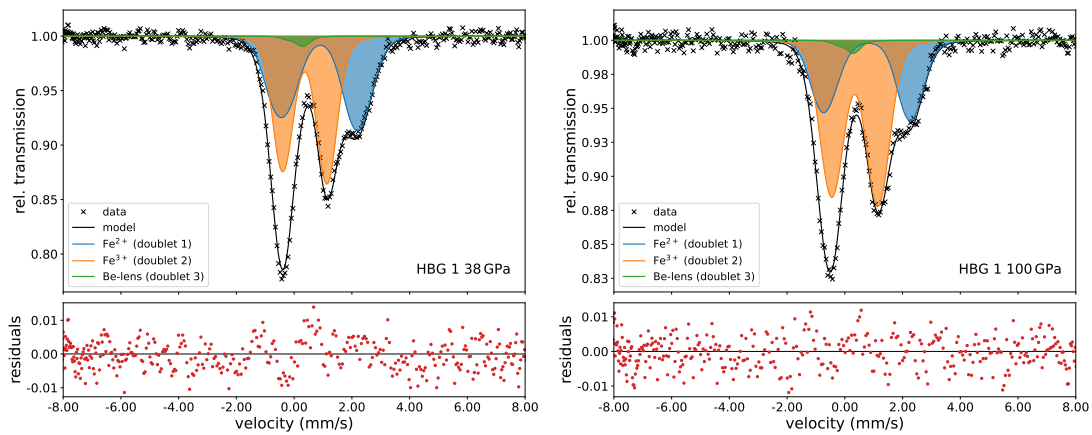


Figure 6.14: SMS spectrum of HBG 1 61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ at **left** 38 GPa and **right** 100 GPa. Black crosses represent the measured data and the black line shows the fitted model. The individual spectral components corresponding to Fe^{2+} (doublet 1), Fe^{3+} (doublet 2), and the Be-lens contribution (doublet 3) are indicated by colored areas. Residuals of the fit are shown in the lower panel.

Between 38 and 100 GPa, the spectral change is small and mainly visible in quadrupole splitting. Generally, The fitted model again reproduces the measured transmission spectrum very well, with residuals that remain randomly distributed around zero. Overall, the spectra demonstrate that the characteristic Mössbauer doublet structure of the glass is preserved over the investigated pressure range up to 100 GPa. While subtle changes in the positions and widths of the absorption features occur with increasing pressure, the relative contributions of the Fe^{2+} and Fe^{3+} doublets remain broadly consistent with the initially high ferric iron fraction of this glass composition.

HBG 2 47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$

Representative SMS spectra of HBG 2 measured at 18 GPa and 118 GPa are shown in Fig. 6.15. In contrast to HBG 1, both spectra show significant differences in comparison to their ambient measurement. At the highest pressure the spectrum inhibits a stark resemblance to the HBG 1. Both isomer shift and quadrupole splitting evolve significantly, indicating changes in the local electronic and structural environment of iron.

HBG 3 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$

Representative SMS spectra of HBG 3 measured at 36 GPa and 102 GPa are shown in

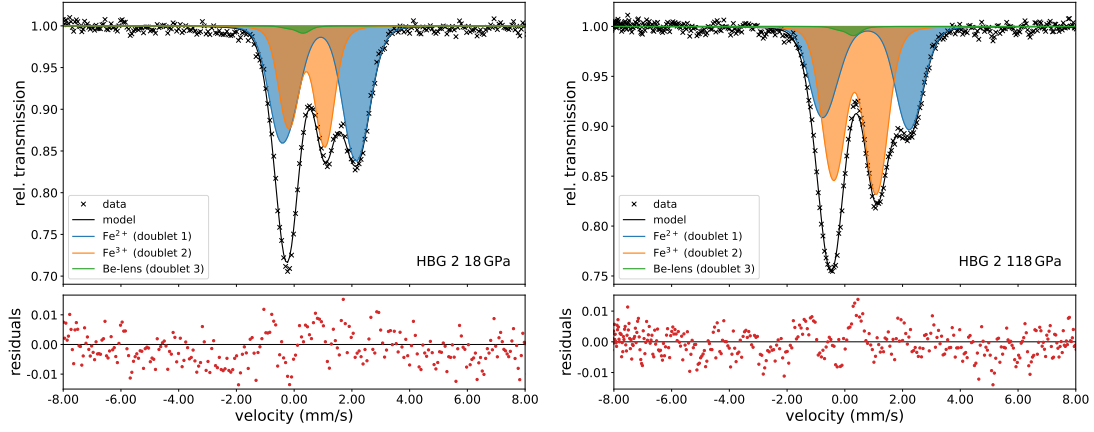


Figure 6.15: SMS spectrum of HBG 2 47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ at **left** 18 GPa and **right** 118 GPa. Black crosses represent the measured data and the black line shows the fitted model. The individual spectral components corresponding to Fe^{2+} (doublet 1), Fe^{3+} (doublet 2), and the Be-lens contribution (doublet 3) are indicated by colored areas. Residuals of the fit are shown in the lower panel.

Fig. 6.16. At the lowest measured pressure at 36 GPa the doublets are nearly balanced, showing a significant difference to the ambient measurement and resembles HBG 2. At the highest pressure of 102 GPa, the spectrum is similar to HBG 1.

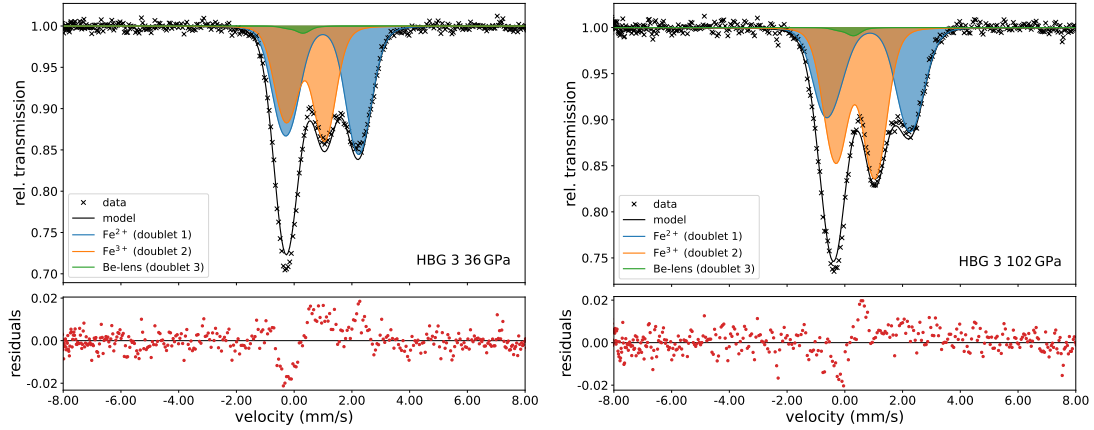


Figure 6.16: SMS spectrum of HBG 3 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ at **left** 36 GPa and **right** 102 GPa. Black crosses represent the measured data and the black line shows the fitted model. The individual spectral components corresponding to Fe^{2+} (doublet 1), Fe^{3+} (doublet 2), and the Be-lens contribution (doublet 3) are indicated by colored areas. Residuals of the fit are shown in the lower panel.

With increasing pressure a trend is visible, which leads to a more unified behavior leaning towards HBG 1. For investigating, if this is the effect of pressure or due to radiation exposure, the following center and off-center position measurements were conducted.

6.4.2.2 Center position vs. off-center position

In addition to the spectra recorded at the center of the sample chamber, several SMS measurements were performed at slightly displaced positions within the sample. These off-center measurements were carried out in order to evaluate potential spatial variations in the sample, which may arise from beam-induced effects, chemical gradients, or redistribution of Fe^{2+} and Fe^{3+} during the HP experiments. Such variations can influence the relative spectral contributions of the Fe^{2+} and Fe^{3+} doublets and therefore affect the derived ferric iron fraction.

Only selected representative spectra are shown in the main text, further center and off-center position spectra are shown in App. A.8.1. A comparison between spectra recorded at the center and slightly off-center positions within the sample chamber at medium pressure (between 61 and 66 GPa) is shown in the following section to illustrate the potential influence of spatial variations on the measured SMS spectra.

The comparison between spectra recorded at the center and slightly displaced positions within the sample chamber reveals differences in the relative contributions of the Fe^{2+} and Fe^{3+} doublets.

For all three glasses, variations in the relative doublet contributions are visible. However, for HBG 1 and HBG 2 these differences remain comparatively small. In contrast, the largest variations are observed for HBG 3, the glass with the lowest $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio. In this case, a pronounced difference between the center and off-center measurements is visible. The off-center spectrum shows a substantially larger contribution of the Fe^{2+} doublet, resulting in a spectral shape that more closely resembles the ambient-pressure spectrum (cf. Fig. 6.12) than the spectrum measured at 36 GPa (cf. Fig. 6.16 left).

The variations in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ contributions observed for HBG 1 and HBG 2 likely reflect minor spatial differences or pressure gradient within the sample chamber. In contrast, the significantly larger differences observed for HBG 3 indicate stronger local variations in the redox state within the sample. These effects may arise from beam-induced oxidation, local chemical heterogeneities, or redistribution of iron species during the HP experiment. Pressure-induced effects are expected to play only a minor role in this context, as the center and off-center spectra were recorded at the same pressure conditions.

6.4.2.3 Evolution of hyperfine parameters with pressure

The representative spectra discussed above demonstrate that the adopted three-doublet model adequately reproduces the measured SMS spectra across the investigated pressure range. From these fits, the hyperfine parameters of the Fe-bearing components, in particular the isomer shift δ and the quadrupole splitting ΔE_Q , were extracted for all spectra.

These parameters provide information about the electronic configuration and the local coordination environment of iron in the glass structure. The isomer shift δ reflects the electron density at the nucleus and is therefore sensitive to the oxidation state and spin-state of iron. In contrast, the quadrupole splitting ΔE_Q arises from the interaction between the nuclear quadrupole moment and the EFG at the nucleus and provides

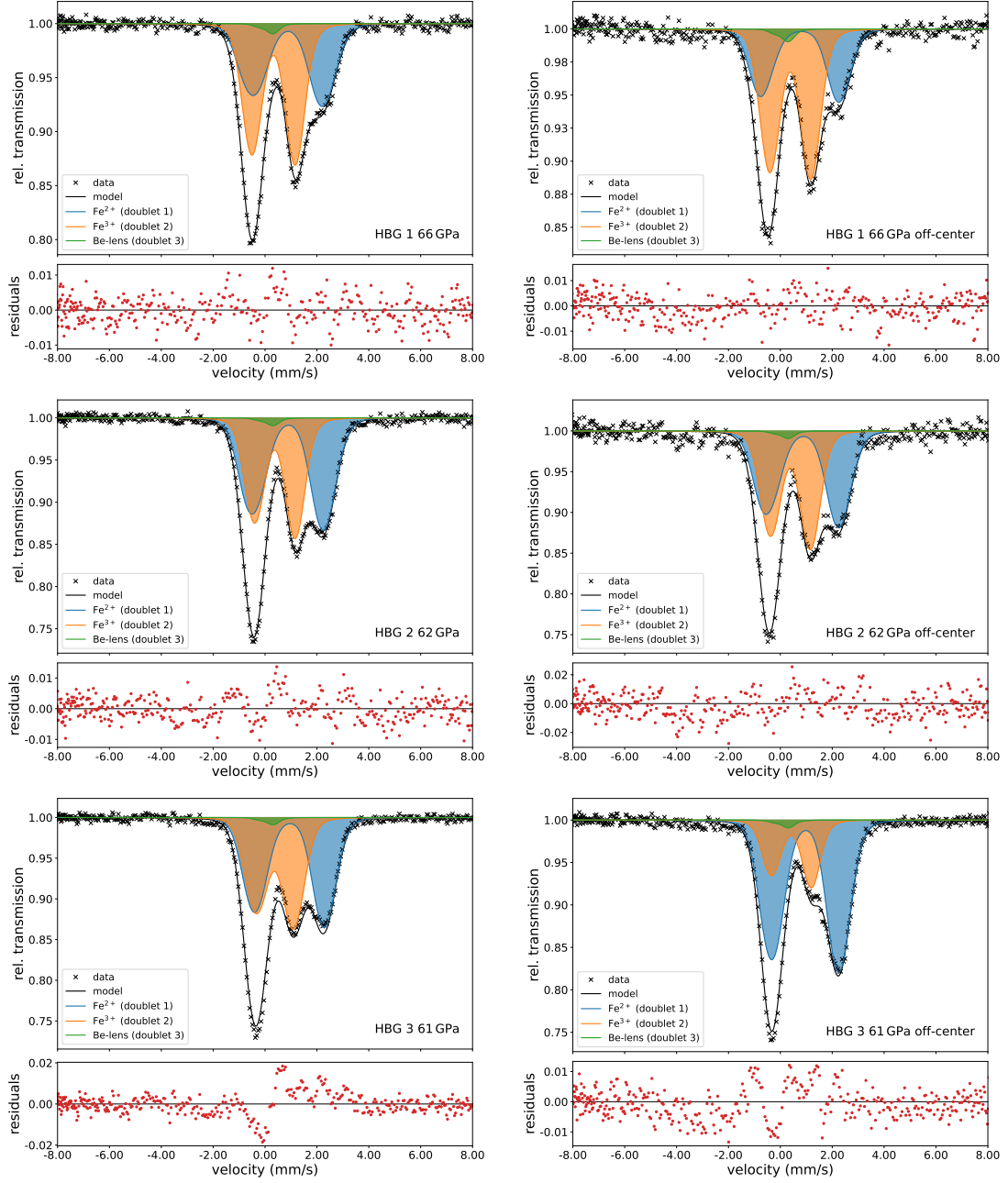


Figure 6.17: Comparison of SMS spectra with the center positions on the **right** and off-center positions on the **left**. At the **top** HBG 1 (61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) at 66 GPa, in the **middle** HBG 2 (47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) at 62 GPa and at the **bottom** HBG 3 (13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) at 61 GPa.

information about the asymmetry of the local coordination environment surrounding the Fe ions.

The pressure dependence of these hyperfine parameters therefore allows the evolution of the electronic and structural environment of iron in the glasses to be evaluated. The ambient data points should be considered with some caution because these spectra were collected from irregular glass fragments outside the DAC, as discussed above.

Isomer shift δ The evolution of the isomer shift δ as a function of pressure for the three HBG glasses is shown in Fig. 6.18. Two distinct groups of values are observed, corresponding to the two fitted doublets. The first doublet exhibits larger isomer shift values between approximately 0.75 and 1.05 mm s^{-1} , while the second doublet shows significantly smaller values around 0.35-0.6 mm s^{-1} . For all three glass compositions, the

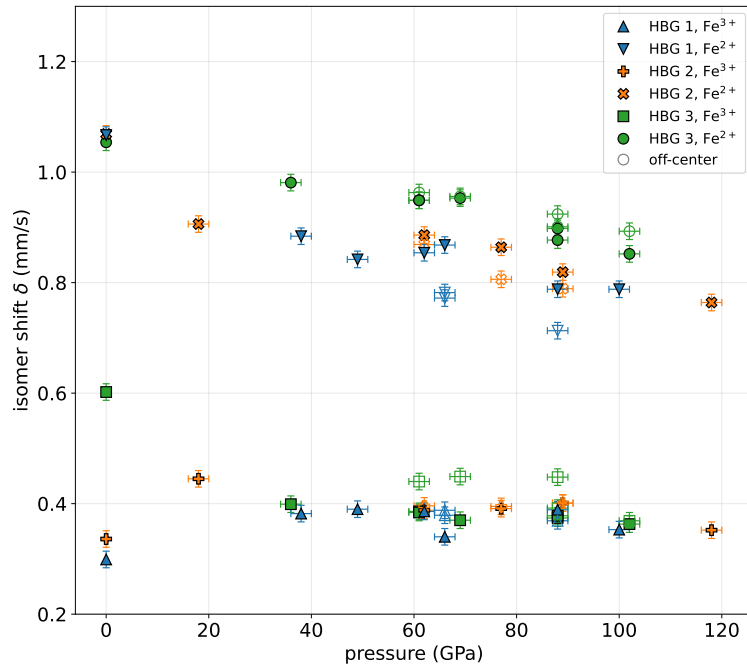


Figure 6.18: Plot of isomer shift δ against pressure for the three HBG samples and divided by doublets for Fe^{2+} and Fe^{3+} . Off-center measurements are indicated by unfilled markers.

isomer shift of both doublets shows a slight overall decrease with increasing pressure. This behavior is consistent with the expected compression of the local Fe-O coordination environment, which increases the electron density overlap between iron and surrounding ligands and thereby reduces the isomer shift. Despite this pressure-induced trend, the separation between the two doublets remains clearly preserved over the entire investigated pressure range up to ~ 120 GPa. The ambient values show different behavior, which may be attributed to the fact, that these samples were outside of a DAC and with varying sizes and thicknesses.

The absolute values of the Fe^{2+} isomer shift differ slightly between the three glasses. The largest δ values are observed for HBG 3, which contains the lowest $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio and is therefore the most reduced composition. In contrast, HBG 1 and HBG 2 exhibit somewhat

lower Fe^{2+} isomer shifts. The Fe^{3+} doublet shows comparatively small variations between the different compositions and remains clustered around $\sim 0.4 \text{ mm s}^{-1}$.

Uncertainties of the isomer shift were estimated as an uncertainty of $\pm 0.015 \text{ mm s}^{-1}$ and are in the reported range from the literature [213, 214]. Pressure uncertainties were estimated to be $\pm 2 \text{ GPa}$.

Some additional scatter in the data arises from spectra recorded at slightly displaced positions on the sample (off-center measurements). These points, indicated by open symbols, seem to follow the general trend, except for the Fe^{3+} isomer shift in HBG 3, which seem relatively stable between 62 and 88 GPa.

Isomer shift for spin-state analysis The isomer shift can serve as a proxy for spin-state determination. For better visualization the Fe^{2+} and Fe^{3+} doublets from Fig. 6.18 are displayed separately in Fig. 6.19 and Fig. 6.20 including areas for the spin-state. The values for the areas were extracted from Gütlich et al. [215].

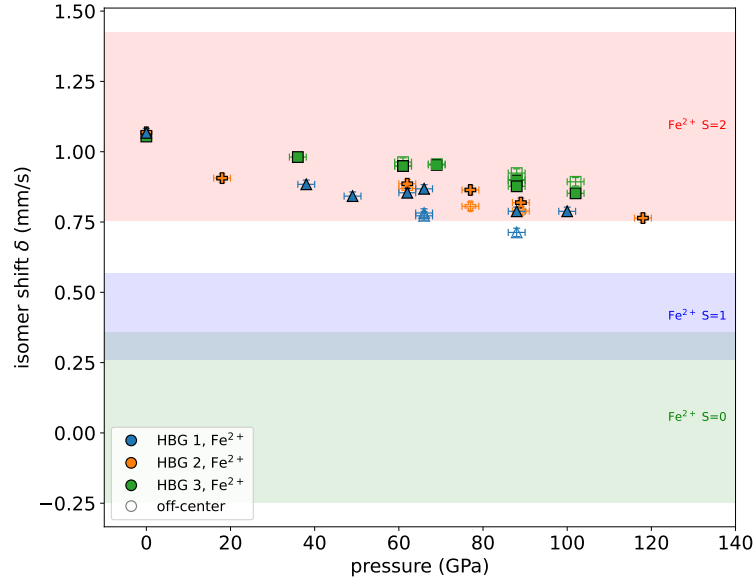


Figure 6.19: Plot of isomer shift δ against pressure for the three HBG samples for their Fe^{2+} doublet and colored areas representing spin-states derived from Gütlich et al. [215]. Off-center measurements are indicated by unfilled markers.

The pressure dependence of the isomer shift for the Fe^{2+} doublet is shown in Fig. 6.19. For all three glasses, the measured δ values range approximately between 0.75 and 1.05 mm s^{-1} over the investigated pressure range. These values fall entirely within the region characteristic for HS Fe^{2+} ($S=2$), as indicated by the shaded reference field derived from Gütlich et al. [215]. A very small systematic shift of the isomer shift values toward the LS regions is observed with increasing pressure. This indicates that Fe^{2+} shows slight changes, but remains in the HS configuration throughout the investigated pressure range. While small variations between the different glasses are visible, all data points remain clearly separated from the regions corresponding to mixed-spin ($S=1$) and LS ($S=0$) Fe^{2+} , supporting the stability of the HS state up to the highest investigated pressures.

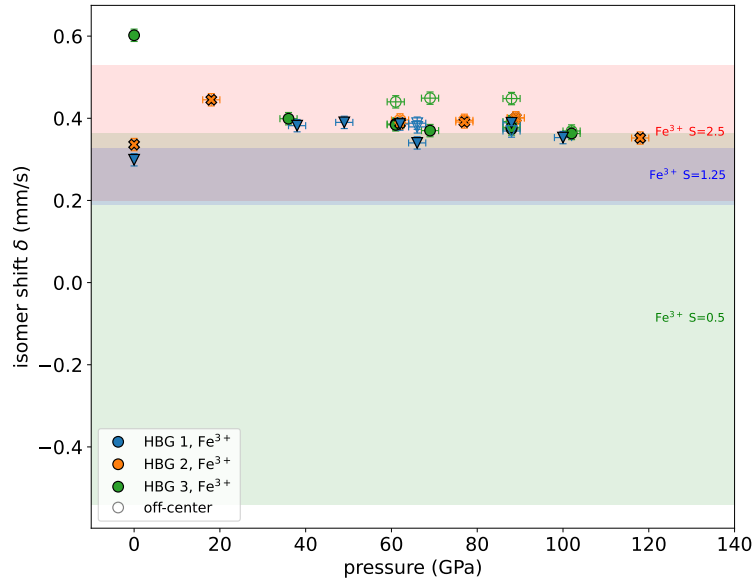


Figure 6.20: Plot of isomer shift δ against pressure for the three HBG samples and their Fe^{3+} doublet and colored areas representing spin-states derived from Gütlich et al. [215]. Off-center measurements are indicated by unfilled markers.

The corresponding isomer shift values for the Fe^{3+} doublet are displayed in Fig. 6.20. In contrast to Fe^{2+} , the δ values for Fe^{3+} cluster around $\sim 0.35\text{--}0.45\text{ mm s}^{-1}$ for all three glass compositions. These values lie within the range typical for HS Fe^{3+} ($S=2.5$), as indicated by the shaded reference field. Similar to the Fe^{2+} data, a slight decrease in δ values is visible, but without an indication of a full spin crossover. The isomer shift values therefore suggest that Fe^{3+} also remains in the HS configuration or might be entering the mixed-spin-state across the investigated pressure range. Minor scatter in the data, including measurements performed at off-center positions within the sample chamber, does not significantly affect this overall interpretation.

Taken together, the isomer shift values indicate that both Fe^{2+} and Fe^{3+} show a slight decrease in spin, but still remain in their respective HS state field reported by Gütlich et al. [215], but since the fields are overlapping, a start of shifting into the reported LS state cannot be excluded.

Quadrupole shift ΔE_Q The evolution of the quadrupole splitting (ΔE_Q) as a function of pressure for the three HBG glasses is shown in Fig. 6.21. Two distinct groups of values are visible, corresponding to the two fitted doublets associated with Fe^{2+} and Fe^{3+} . The Fe^{2+} doublet consistently exhibits larger quadrupole splitting values, ranging from approximately 1.0 to 1.5 mm s^{-1} across the investigated pressure range. In contrast, the Fe^{3+} doublet shows significantly smaller values between roughly 0.4 and 0.8 mm s^{-1} .

For all three glass compositions, a gradual and slight increase in ΔE_Q with increasing pressure can be observed for the Fe^{2+} component. This trend suggests an increasing asymmetry of the electric field gradient at the Fe nucleus with compression of the local coordination environment. The Fe^{3+} component also shows moderate variations

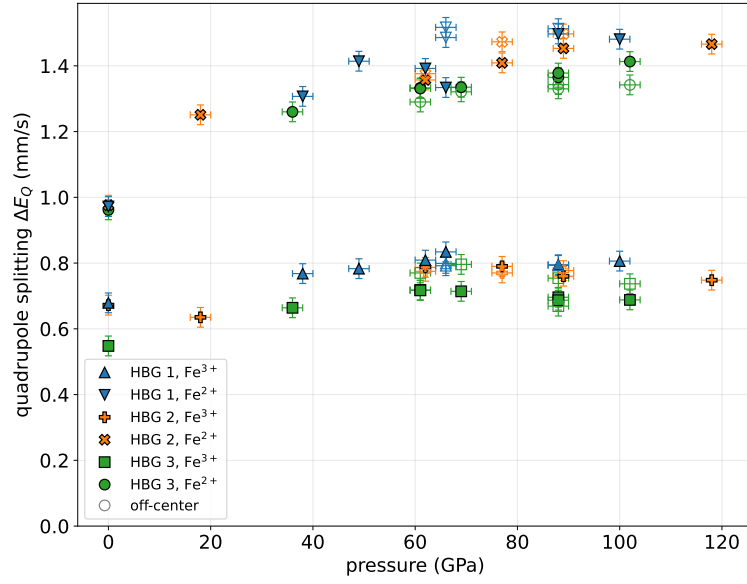


Figure 6.21: Plot of quadrupole shift ΔE_Q against pressure for the three HBG samples separated by the Fe^{2+} and Fe^{3+} doublets. Off-center measurements are indicated by unfilled markers.

with pressure, although the overall changes are smaller compared to those observed for Fe^{2+} and remain at approximately the same values after 60 GPa. Uncertainties of the quadrupole splitting were estimated to an uncertainty of $\pm 0.03 \text{ mm s}^{-1}$ for ΔE_Q and lie within the literature range [214]. Pressure uncertainties were estimated to be $\pm 2 \text{ GPa}$.

The three glass compositions display similar pressure-dependent trends, while small offsets between the datasets reflect differences in their initial $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios and possibly local structural environments. Additional scatter in the data is associated with spectra measured at slightly displaced positions within the sample chamber (off-center measurements). These measurements generally follow the same overall trends as the center spectra and therefore do not significantly affect the interpretation of the pressure dependence of the quadrupole splitting.

Overall, the observed increase in ΔE_Q with pressure indicates progressive distortion of the local Fe coordination environment in the compressed glass structure while maintaining the separation between the Fe^{2+} and Fe^{3+} components throughout the investigated pressure range.

Isomer shift δ and Quadrupole shift ΔE_Q for Fe-coordination The Fe^{3+} doublets plot consistently within the field of sixfold coordination (octahedral) for all samples and across the entire pressure range, indicating no major structural change. Only the ambient HBG 3 is located near the lower boundary of the $\text{Fe}^{2.5+}$ field for the Fe^{3+} doublet. Important to note is, that the isomer shift and quadrupole splitting for ambient Fe^{3+} would be expected to be within the tetrahedral coordination (fourfold) and evolve to octahedral with increasing pressure. But according to Weigel et al. [21], iron-bearing glasses can contain non-tetrahedral Fe^{3+} .

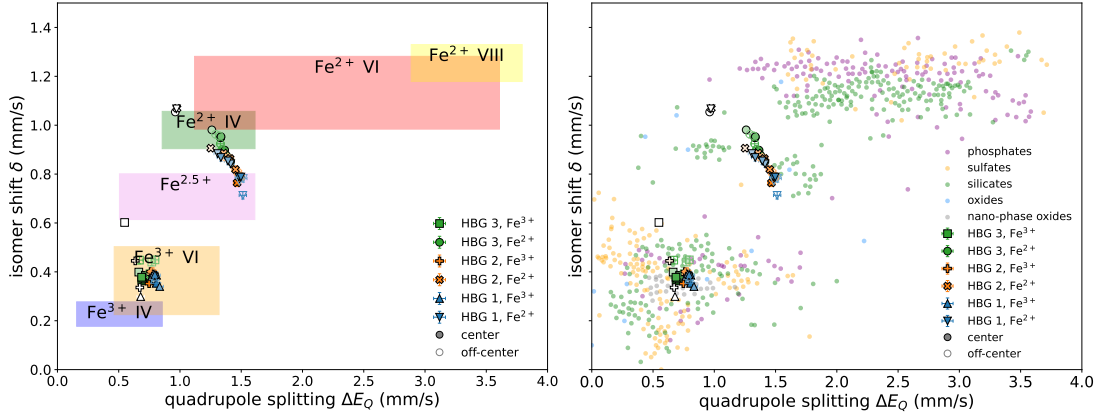


Figure 6.22: Plot of isomer shift δ against quadrupole shift ΔE_Q after Fig. 6.1 derived from Dyar and Sklute [99] for the three HBG samples separated by the Fe^{2+} and Fe^{3+} doublets. Off-center measurements are indicated by unfilled markers with the samples equivalent color as edge color, and with increasing pressure, the marker is more intensely filled. **Left)** coordination fields in combination with the here discussed data. **Right)** Roughly extracted data from Dyar and Sklute [99] (less saturated) in combination with the here discussed data. The data points from this study are the same for the left and right.

In contrast, the Fe^{2+} doublets exhibit a systematic pressure-dependent trend. With increasing pressure, the data shift from the field of fourfold coordination toward the $\text{Fe}^{2.5+}$ region. This behavior is observed consistently for all three samples and suggests a gradual modification of the local coordination environment of Fe^{2+} under compression.

Comparison with the digitized dataset of Dyar and Sklute (Fig. 6.22, right) shows that the Fe^{2+} doublets fall within the range of silicate compositions and Fe^{3+} doublets overlap with data from silicates, phosphates and nano-phase oxides.

6.4.2.4 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio calculation

The pressure dependence of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ derived from the fitted SMS doublet intensities is shown in Fig. 6.23 for the three HBG glasses. The calculated values are summarized in Tables A.10-A.12 in the Appendix. Overall, the three glasses display distinct redox behavior that reflects their different initial $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios. Uncertainties in the ferric fraction $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ were estimated to be ± 0.05 , while pressure uncertainties were estimated to be ± 2 GPa.

For HBG 1, which initially contains the highest ferric iron fraction (61%), the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio calculated from the ambient SMS spectrum (64%) is in very good agreement with the WCCA-derived value. The calculated ferric fraction remains relatively stable over the entire investigated pressure range, fluctuating between approximately 54 and 66% without showing a systematic trend with increasing pressure. Minor variations are observed between measurements performed at the center and slightly displaced positions within the sample chamber, but the overall ferric fraction remains broadly consistent with the initially oxidized character of this glass. Overall, the calculated $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios vary by approximately $\pm 10\%$ relative to the WCCA-derived value.

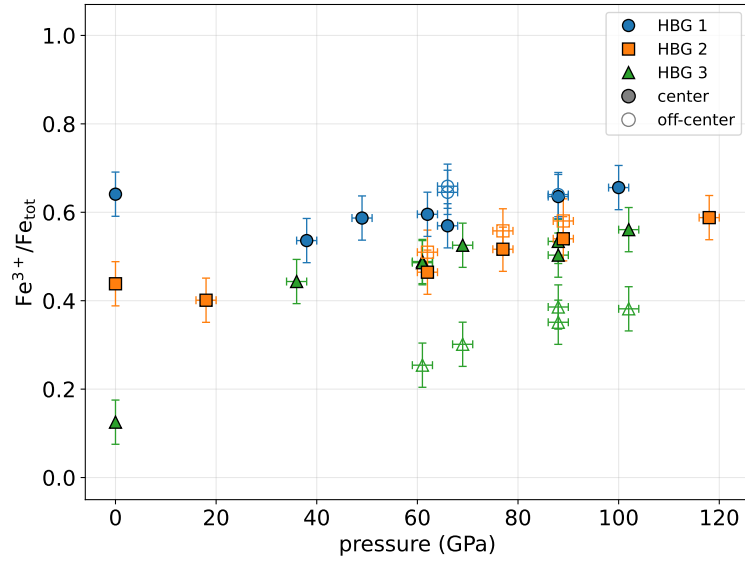


Figure 6.23: Calculated $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ as a function of pressure for the three HBG samples. Off-center measurements are indicated by darker markers in the corresponding sample colors.

HBG 2 exhibits intermediate $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ values, reflecting its lower initial ferric iron content (47%). At ambient conditions the ferric fraction derived from SMS is approximately 51% and decreases slightly at low pressures before gradually increasing again with pressure. At the highest investigated pressures, $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ reaches values of approximately 55-59%. Overall, the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios derived from the SMS fits range between 40 and 59%, corresponding to a relative variation of approximately -15% to $+25\%$ compared to the WCCA-derived value of 47%. Similar to HBG 1, small variations between center and off-center measurements are observed but do not significantly affect the overall trend.

The largest variations are observed for HBG 3, which initially contains only a small ferric iron fraction (13%). At ambient conditions the SMS-derived value (12.53%) is in very good agreement with the WCCA. With increasing pressure, however, the ferric fraction increases significantly in the center measurements, reaching values of approximately 53-56% at pressures above ~ 70 GPa. In contrast, spectra measured at off-center positions show substantially lower $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ values of approximately 35-39%, indicating strong spatial variations within the sample chamber for this composition. Quantitatively, the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios derived from center measurements correspond to an increase of approximately $+238\%$ to $+331\%$ relative to the WCCA-derived value, whereas the off-center measurements correspond to an increase of about $+92\%$ to $+200\%$. Both sets of measurements therefore show significant deviations from the initial composition, although the center measurements clearly exhibit stronger changes.

Despite these variations, the overall data indicate that the ferric iron fraction generally increases with pressure for the more reduced glasses, whereas the more oxidized compositions remain comparatively stable. This effect is particularly pronounced for HBG 3, which shows a substantial increase in Fe^{3+} content.

The observed behavior for HBG 3 cannot be explained by pressure effects alone. Possible explanations include beam-induced oxidation or radiation-driven modifications of the

iron coordination environment during the high-pressure experiments.

6.4.3 X-ray emission spectroscopy results

In the following, the findings from XES for the three HBG samples are presented. During the second experiment, HBG 3 was remeasured together with Fe^{2+} and Fe^{3+} reference materials. Selected XES spectra are shown alongside the IAD and M1 analyses.

As discussed in Chap. 6.3.2.1, the data must be interpreted with caution.

6.4.3.1 $\text{K}\beta_{1,3}$ emission spectra

Due to the large number of XES spectra, only selected pressures are shown here. The spectra are shifted to the same CMS of 7055 eV for the IAD analysis (Chap. 6.4.3.2).

HBG 1

HBG 1 (cf. Fig. 6.24 left)) between 27 to 120 GPa inhibits a reduction of the $\text{K}\beta''$ peak, whereas a shift to lower energies for the $\text{K}\beta_{1,3}$ peak is not visible, which would support a decrease in spin-state. At 37 GPa, the spectrum shows pronounced deviations for which no clear explanation is available. Similar anomalous behavior is observed sporadically across both experiments, for both analyzer crystals and all samples, further complicating the interpretation.

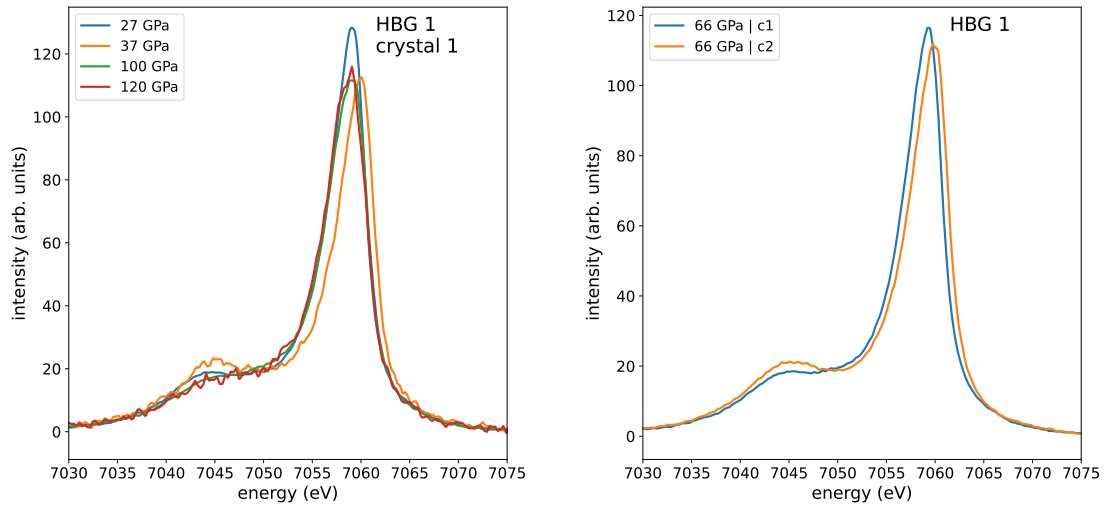


Figure 6.24: $\text{K}\beta_{1,3}$ spectra for HBG 1 61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ **left**) at different pressures for crystal 1 **right**) comparison between crystal 1 and crystal 2.

A comparison between analyzer crystals 1 and 2 (Fig. 6.24, right) reveals significant differences in spectral shape. These differences mimic features typically associated with a spin transition. However, both spectra were collected at the same pressure (66 GPa) and thus do not reflect intrinsic sample behavior. These discrepancies affect CMS shifting and area normalization, and therefore directly influence the interpretation of spin-state evolution.

In the following, only spectra from analyzer crystal 1 are shown. Comparisons between both analyzer crystals for the other samples are provided in Appendix Fig. A.38.

HBG 2

The pressure-dependent behavior of HBG 2 (Fig. 6.25) shows a gradual decrease of the $\text{K}\beta''$ peak from 18 GPa up to 109 GPa, with the exception of the spectrum at 58 GPa.

This trend may indicate a progressive change in spin-state with increasing pressure.

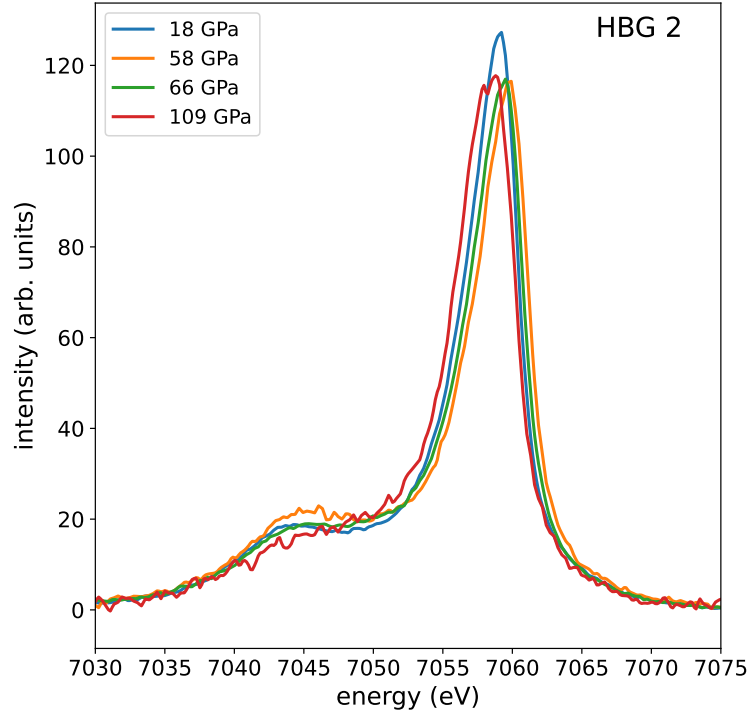


Figure 6.25: $\text{K}\beta_{1,3}$ spectra for HBG 2 47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ at different pressures.

HBG 3

The spectra of HBG 3 from both experiments are shown in Fig. 6.26. Two main observations can be made:

First, the spectral shapes differ between the two experiments at comparable pressures. In particular, the $\text{K}\beta''$ peak in the second experiment (Fig. 6.26, right) is more pronounced, especially at 49 GPa.

Second, both datasets show a gradual decrease of the $\text{K}\beta''$ peak and a shift of the $\text{K}\beta_{1,3}$ peak towards lower energies with increasing pressure, consistent with a spin transition. However, inconsistencies remain: for example, at 65 GPa in the first experiment, the spectra exhibit a stronger LS character than at 104 GPa in the second experiment.

Overall, at the highest pressures reached for each HBG sample, the spectra converge towards a similar shape, characterized by a comparable degree of $\text{K}\beta''$ peak reduction.

Fe^{2+} reference and Fe^{3+} reference

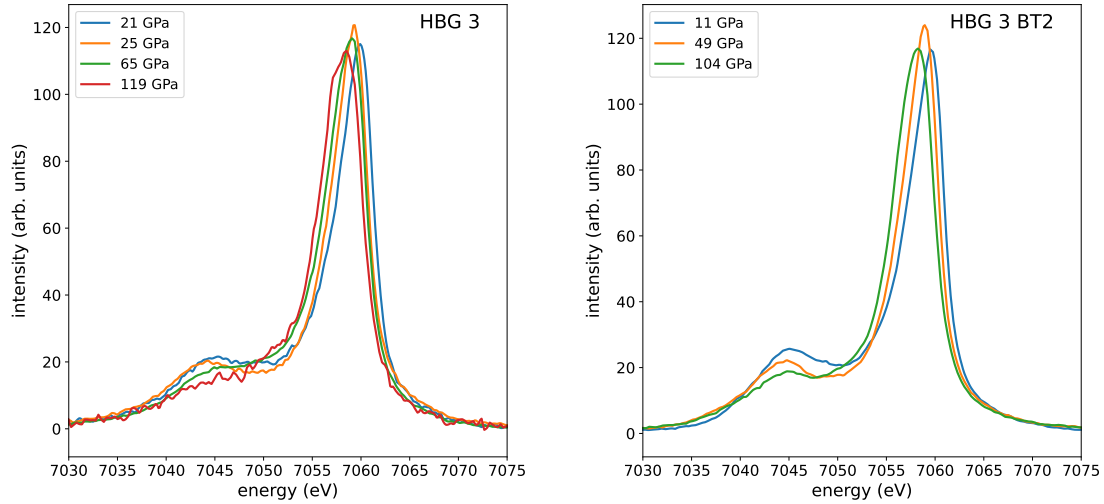


Figure 6.26: $K\beta_{1,3}$ spectra for HBG 3 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ at different pressures **left)** first experiment **right)** second experiment.

The Fe^{2+} reference spectra (Fig. 6.27, left) show only minor changes with increasing pressure up to 115 GPa, arguing against a significant spin transition.

In contrast, the Fe^{3+} reference spectra (Fig. 6.27, right) display a pronounced reduction of the $K\beta''$ peak and a shift of the $K\beta_{1,3}$ peak towards lower energies between 10 and 118 GPa, consistent with a transition from HS to LS state.

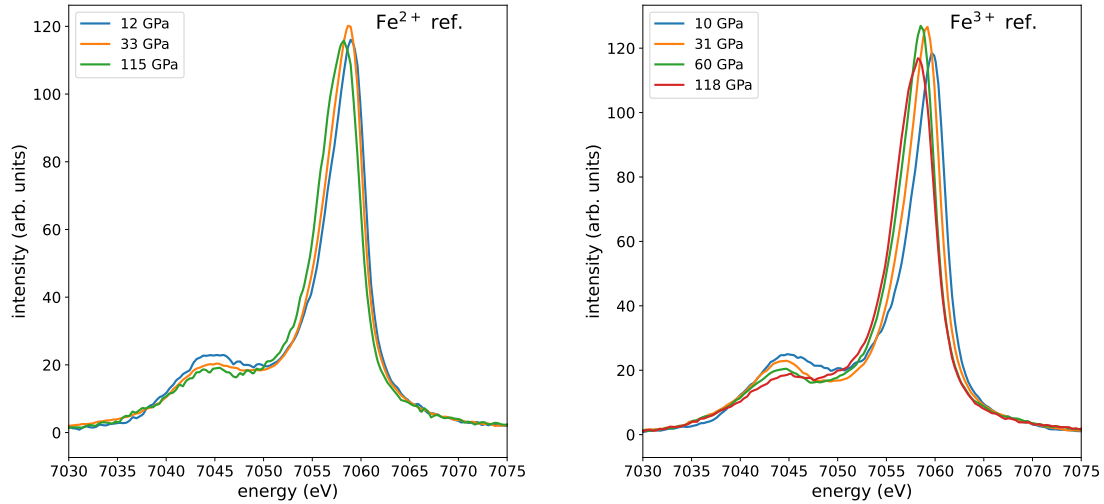


Figure 6.27: $K\beta_{1,3}$ spectra at different pressures for **left)** Fe^{2+} reference and **right)** Fe^{3+} reference.

Comparison of HBG 1-3 at their highest pressure

In Fig. 6.28 are the three HBGs shown at their highest pressure. This allows for a better comparison of their similarities. For crystal 1, only slight differences between the spectra of all the samples are visible. The spectra of crystal 2 for HBG 2 and HBG 3 are nearly identical. Since the spectral shapes of both crystals and samples have a stark

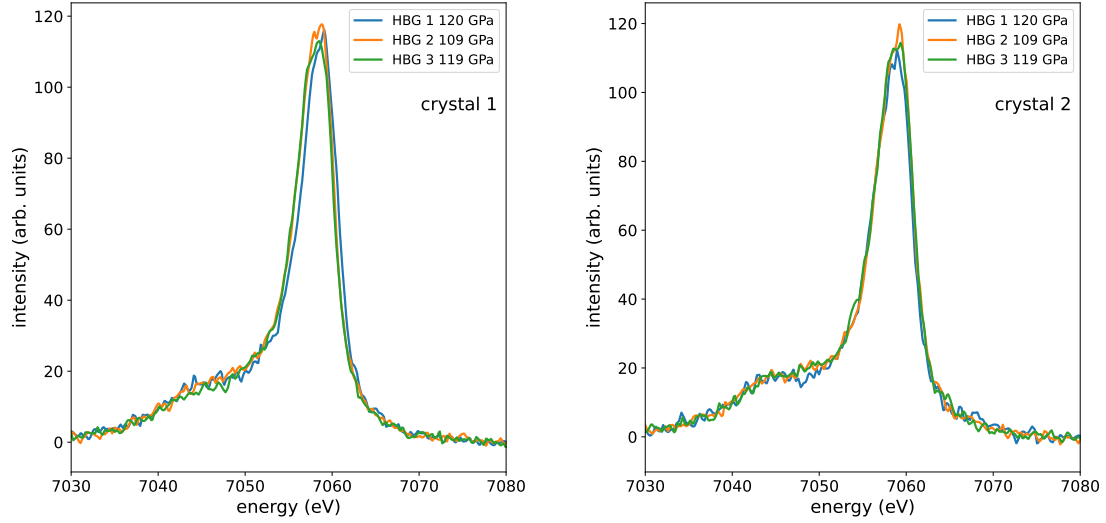


Figure 6.28: $\text{K}\beta_{1,3}$ spectra for HBG 1-3 at their highest pressure for **left)** crystal 1 and **right)** crystal 2.

resemblance, the assumption of an increase in $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ seen in the SMS results (cf. Sec. 6.4.2.4), might be reflected here.

The HBG samples from the first experiment show behavior more similar to the Fe^{3+} reference, whereas HBG 3 from the second experiment exhibits features closer to the Fe^{2+} reference.

For a qualitative assessment of the spin-state evolution at high pressure, the following analyses were performed.

6.4.3.2 IAD results

The IAD analysis follows the procedure described in Chap. 5.4. The calculated IAD values for the three HBG samples from both experiments are shown in Fig. 6.29, separated by analyzer crystal. The samples respective maximum pressure was used as a reference for the LS state.

As noted above, spectral shape variations occur irregularly across pressure series and independently of sample or analyzer crystal. These variations complicate CMS determination and spectral alignment, and are reflected in the calculated IAD values. Furthermore, no clear LS state reference spectrum was measured during the experiments. Therefore, the highest-pressure spectrum of each sample was used as a reference, resulting in an IAD value of zero by definition. Consequently, the second-highest pressure point is used to describe trends in spin-state evolution. All calculated IAD values can be found in the Appendix in Tab. A.13 – Tab. A.18. As an error 20% of the highest of IAD values (0.3407 HBG 2), which corresponds to 0.068, was estimated and used for all samples.

For **HBG 1** in Fig. 6.29 top left), a trend of decreasing IAD value with pressure for the second crystal is visible starting at an IAD value of 0.17 and ending at an IAD value of 0.05 at 110 GPa. For the second crystal is trend could be assumed aswell, when the two

lowest pressures at 27 and 33 GPa are ruled out. Then the IAD would be starting at a value of 0.25 at 37 GPa decreasing to an IAD value of 0.07 at 110 GPa.

A clearer distinction for IAD value development is observable in **HBG 2** (cf. Fig. 6.29 top right)) with a high degree of difference between analyzer crystal 1 and 2. The emission signal focused from crystal 1 shows a gradual decrease of IAD value from 0.13 at 18 GPa, 0.32 at 23 GPa to 0.13 at 98 GPa. The trend provided by the second analyzer crystal is shows more a fluctuation around an IAD value of roughly 0.1, with the exception for the highest pressure, which was used as a LS state reference. So the results for HBG 2 are more ambiguous.

HBG 3 from the first experiment in Fig. 6.29 bottom left), shows a gradual decrease in IAD value for the emission from both analyzer crystals, but with a different degree of manifestation. The IAD value from the first analyzer crystals decreases from 0.32 to 0.06 between 21 and 106 GPa, whereas the IAD value of the second crystal decreases from 0.1 to 0.04 in the same pressure range. Important to note is a fluctuation of IAD values between 21 and 49 GPa for the first analyzer crystal. The second experiment shows the same behavior in decreasing IAD value as well. For the first crystal three regions are visible with a high IAD value between 11 and 40 GPa (~ 0.27), a medium IAD value (~ 0.12) between 49 and 67 GPa and a low IAD value (~ 0.02) region from 78 to 95 GPa. Roughly the same regions are visible for the second analyzer crystal, but with different behavior, where the medium pressure region from 40 to 67 GPa show the highest IAD values.

A more coherent behavior is observable for the **Fe²⁺ reference** (cf. Fig. 6.30 left)), where there seem to be simply an offset between both crystals, but the evolution in IAD value are in good agreement. The starting value of IAD of 0.19 and 0.15 for crystal 1 and 2 at 12 GPa, respectively follow a gradual decrease to values of 0.02 at 106 GPa.

The evolution of IAD values with increasing pressure for the **Fe³⁺ reference** in Fig. 6.30 right) again shows different behaviors between both crystals. For the first analyzer crystals' pressure-dependent evolution a gradual decrease of IAD values is visible from 0.32 at 10 GPa to 0.05 at 111 GPa. The emission signal from the second analyzer crystal has a comparable IAD value of 0.30 to crystals one at the lowest pressure, then a sharp drop at 20 GPa to an IAD value of 0.12, where it fluctuates until a further gradual decrease after 88 GPa to an IAD of 0.02 at 111 GPa.

The calculated IAD values emphasize the need for a careful handling of especially the CMS shifted XES spectra. For this reason, the M1 analysis presented in the following section is considered to be more robust, as it explicitly does not rely on CMS alignment [161].

6.4.3.3 First moment results

The results on the M1 energy positions are presented in Fig. 6.31 for the HBG sample from both experiments and Fig. 6.32 shows the Fe²⁺ and Fe³⁺ reference from the second experiment. The error for the M1 position was estimated as 0.1 eV. The M1 energy position provides an alternative metric to track electronic and spin-state changes that does not rely on cms alignment. This makes it less sensitive to the spectral distortions

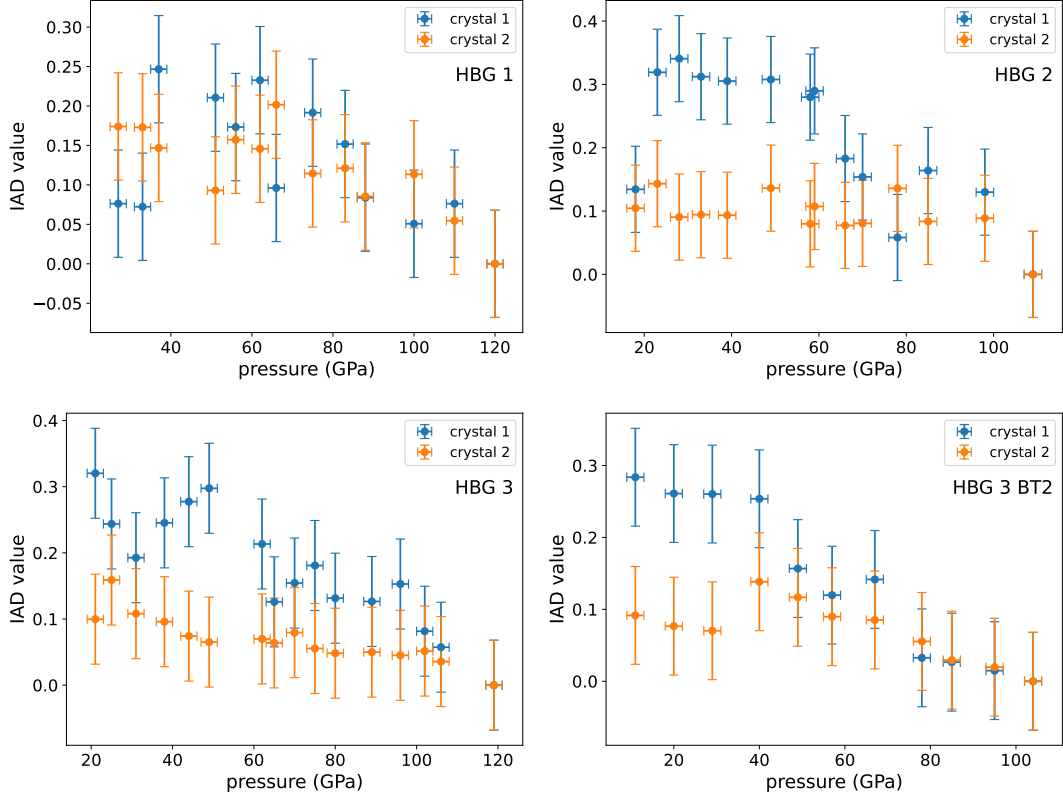


Figure 6.29: IAD values with pressure for the HBG samples for each analyzer crystal. **top left)** HBG 1, 61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$; **top right)** HBG 2, 47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$; **bottom left)** HBG 3, 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$; **bottom right)** HBG 3 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ at the second experiment.

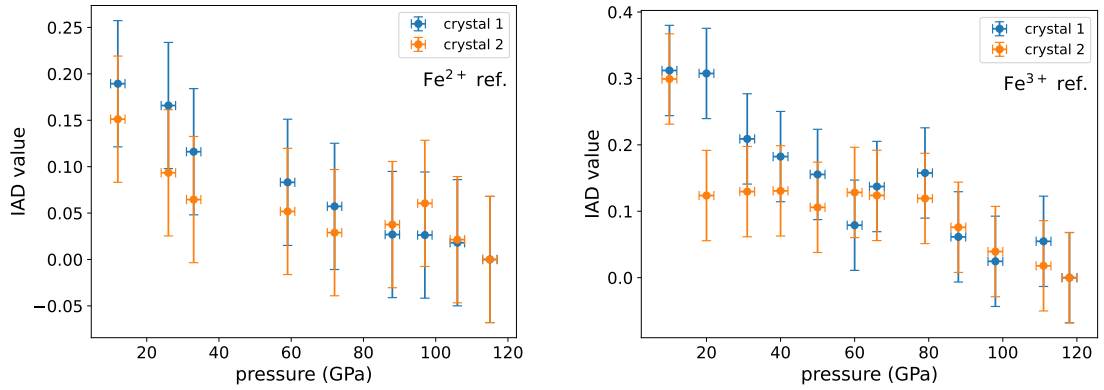


Figure 6.30: IAD values with pressure for **left)** Fe^{2+} reference and **right)** Fe^{3+} reference for each analyzer crystal.

discussed above and therefore potentially more robust for evaluating pressure-induced changes in spin-state.

A systematic offset between analyzer crystals 1 and 2 is observed for all samples. Notably, the direction of this offset is reversed between the first and second experiment. This inversion indicates that the offset is not intrinsic to the samples but instead reflects energy calibration issues.

Across all HBG samples and reference materials, the M1 energy position shows a systematic shift towards lower energies with increasing pressure. This trend is observed consistently for both analyzer crystals and in both experimental runs. This behavior under compression shows a gradual decrease in spin, but do not yet confirm a full HS to LS transition. While the absolute M1 values differ between crystals, the pressure-dependent trends remain consistent.

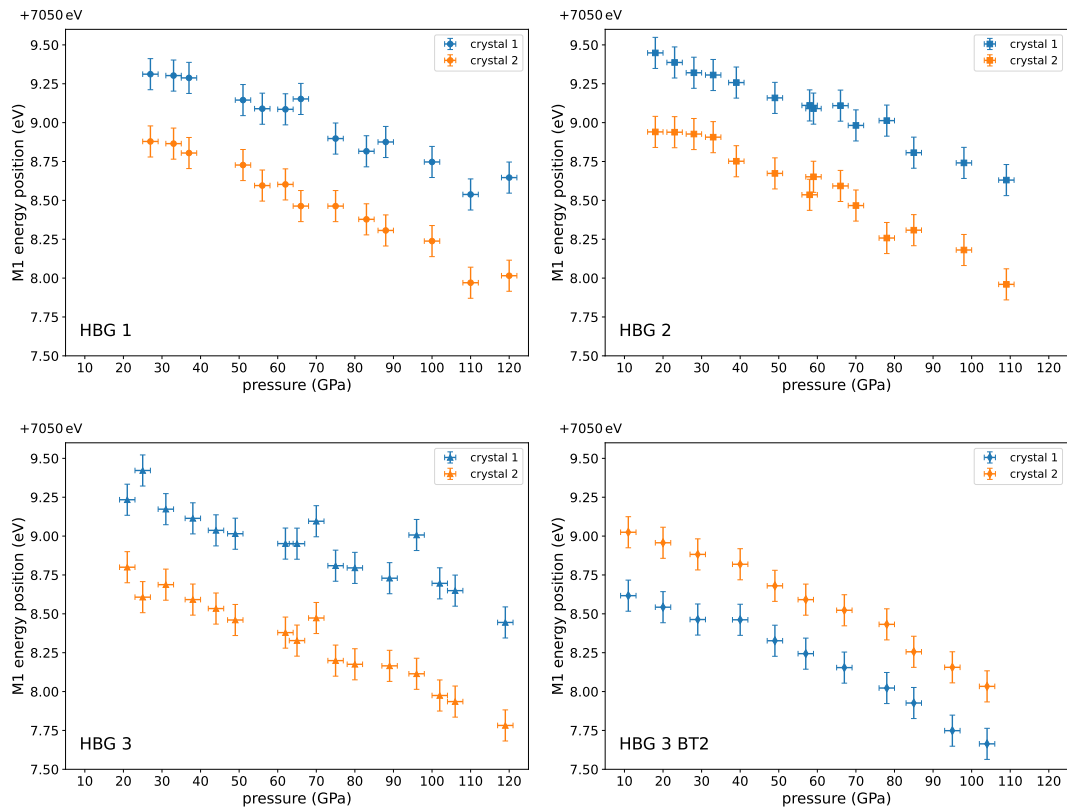


Figure 6.31: M1 energy positions with pressure for the HBG samples for each analyzer crystal. **top left)** HBG 1, 61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. **top right)** HBG 2, 47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. **bottom left)** HBG 3, 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. **bottom right)** HBG 3 13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ at the second experiment.

All HBG datasets evolve toward lower M1 energies with pressure, following trajectories that are broadly consistent with a reduction in average spin-state. However, because the glasses contain mixed valence iron and inhabit no long-range order, the derived spin values should be regarded as qualitative rather than quantitative.

Since the gradual development is reflected in all measurements, the M1 positions vary. To place the observed pressure-induced M1 shifts into a broader context, the measured

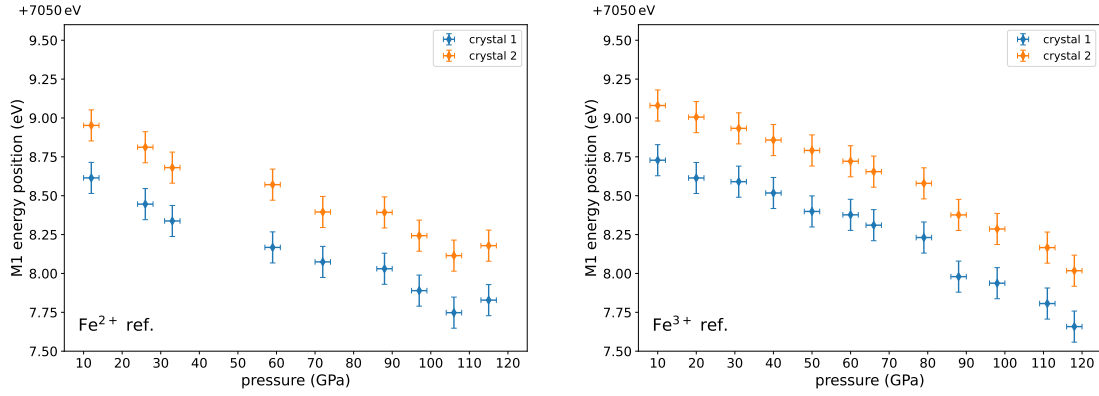


Figure 6.32: M1 energy positions with pressure for **left)** Fe^{2+} reference and **right)** Fe^{3+} reference for each analyzer crystal.

M1 positions were compared with literature values for iron-bearing compounds with known oxidation and spin-states. Although the calibration is necessarily approximate because of differences in composition and local coordination environment, it provides a qualitative framework for interpreting the direction and magnitude of the observed shifts.

Lafuerza et al. [28] reported M1 energy positions for a range of iron-bearing reference compounds covering different oxidation and spin-states. These reference values define an approximately linear relationship between M1 energy position and spin-state, which can be used as a calibration. Based on this calibration, the measured M1 positions in this study were shifted to literature reference values via extrapolation for 0 GPa of each dataset. This procedure preserves the relative pressure evolution while enabling comparison between different samples and experimental runs. The HBG samples were assigned as the following at 0 GPa: HBG 1 to 7059.56 eV ($S = 2.305$), HBG 2 to 7059.52 eV ($S = 2.235$), HBG 3 to 7059.43 eV ($S = 2.065$), consistent with their mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ character as an approximation. The Fe^{2+} reference was anchored to FeO at 7059.39 eV ($S = 2$), and the Fe^{3+} reference to Fe_2O_3 at 7059.67 eV ($S = 2.5$). The resulting shifted M1 positions, together with their corresponding spin estimates based on the literature calibration, are shown in Fig. 6.33 for both analyzer crystals. This approach provides an estimate of spin-state evolution with pressure.

M1 positions and calculated spins for each sample and pressure are provided in the Appendix in Tab. A.19 – Tab. A.24 as well as in Fig. A.39.

All datasets in Fig. 6.33 show a systematic decrease in M1 energy position with increasing pressure, indicating a progressive reduction in spin-state. At first glance, this seems consistent, nevertheless, Fe^{2+} and Fe^{3+} references are expected to behave differently. Further, the XES data suggests a (nearly) full LS state of the composition including the ferrous and ferric iron. This behavior is not visible in the SMS data. Due to the beforehand mentioned challenges with the XES setup, especially the detector, no definitive statement is possible and therefore the XES results will not be considered in the following discussion.

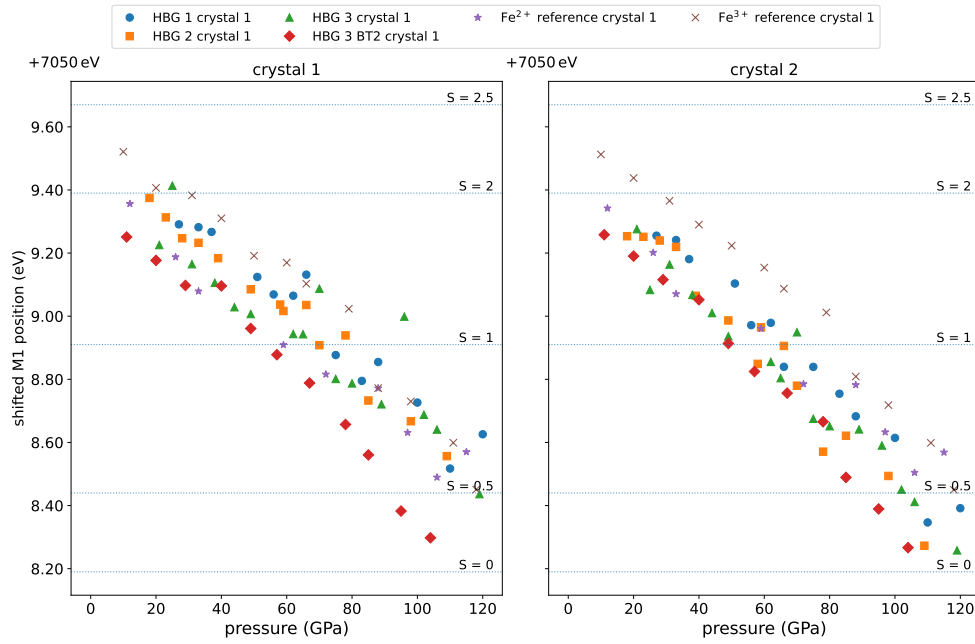


Figure 6.33: Pressure-dependent shifted M1 positions for all measured samples from two experiments with spin approximation based on M1 positions from different samples of varying oxidation and spin-state published from Lafuerza et al. [28]. Results obtained via **left**) analyzer crystal and **right**) analyzer crystal two.

6.5 Discussion

The interpretation of the data is complex due to multiple processes occurring simultaneously during compression. The results are discussed below in the context of current literature and their implications for iron behavior in silicate glasses at high pressure. The XES data is not considered in the following as explained in the chapter beforehand.

6.5.1 Structural disorder and spectroscopic interpretation

A key distinction between glasses and crystals is that glasses exhibit continuous distributions of sites rather than discrete crystallographic sites. Consequently, spectroscopic observables such as Mössbauer hyperfine parameters and XANES pre-edge features represent averages over heterogeneous local environments [99, 208]. The parameter fields associated with Fe^{2+} and Fe^{3+} across different coordinations can overlap, making coordination and spin-state assignments from small parameter shifts inherently ambiguous in disordered materials [99]. The interpretation of the SMS spectra further depends on the adopted fitting model. The use of two doublets to represent Fe^{2+} and Fe^{3+} necessarily simplifies a potentially continuous distribution of local environments in the glass and also the potential occurrence of Fe^{2+} and Fe^{3+} LS doublets. As a result, changes in fitted component areas may partly reflect redistribution within a broadened population of Fe sites rather than strictly discrete changes in oxidation state. This limitation must be considered when interpreting pressure-dependent variations in $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$.

For HBG under pressure, densification and coordination changes can shift hyperfine parameters even in the absence of a discrete electronic transition, while increasing structural heterogeneity leads to broadened parameter distributions [20, 99].

Finally, glasses remain metastable and kinetically arrested states, and relaxation effects can influence derived structural populations in ways that differ from fully molten systems [209]. These factors must be considered when interpreting spectroscopic parameters and fitted component distributions in compressed silicate glasses.

6.5.2 Overview of pressure-dependent behavior in HBG glasses

The combined SMS datasets reveal that compression affects the three haplobasaltic glasses in a systematic but composition-dependent manner. While the initial ambient-pressure spectra from SMS reflect the distinct $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios of the samples in agreement with the XANES and WCCA characterization, the spectral differences between HBG 1, HBG 2, and HBG 3 progressively diminish with increasing pressure. At the highest pressures investigated, the SMS spectra of all three compositions show similar relative contributions of the fitted doublets.

At the same time, the pressure evolution of the derived $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios differs markedly between the samples. HBG 1, which is initially the most oxidized composition, remains comparatively stable over the investigated pressure range. In contrast, HBG 2 and especially HBG 3 show a pronounced increase in the ferric fraction derived from SMS fits. For HBG 2, center and off-center measurements differ only slightly, whereas in HBG 3 this effect is strongest in center measurements and weaker in off-center spectra.

This trend qualitatively resembles the pressure-induced stabilization of Fe^{3+} observed in high-pressure melt experiments, where Fe^{2+} can disproportionate via electron hopping into Fe^{3+} and metallic Fe [216, 217]. However, the experimental conditions of the present study differ fundamentally from those of high-temperature melt experiments. In particular, disproportionation reactions require atomic mobility and phase separation, including the formation of metallic Fe, which are not expected under cold-compression conditions in a diamond anvil cell.

Moreover, the pronounced spatial variability between center and off-center measurements, especially in HBG 3, demonstrates that the derived $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios are sensitive to local conditions and do not represent a homogeneous bulk property. This observation is inconsistent with a pressure-driven redox reaction and might be an effect of radiation.

Previous high-pressure Mössbauer studies of silicate glasses have reported similar increases in the relative spectral area of Fe^{3+} with pressure [190]. However, the origin of this effect remains ambiguous and may reflect differences in recoil-free fractions, pressure-induced structural changes, or redistribution of spectral weight among Fe-bearing environments, rather than a true change in oxidation state. In addition, experimental and theoretical work suggests that charge transfer between Fe^{2+} and Fe^{3+} is not readily activated at ambient temperature [193].

Furthermore, MOCT processes can modify the electronic structure of iron through partial electron delocalization between Fe $3d$ and O $2p$ orbitals. Such effects are particularly relevant in disordered systems and can influence spectroscopic observables without requiring a change in formal oxidation state [205, 206]. Consequently, variations in

fitted spectral components may reflect evolving site distributions and electronic structure rather than a true bulk redox change.

Taken together, these observations indicate that the (apparent) increase in $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ can be interpreted as an effect arising from pressure-induced modifications of local coordination, site distortion, and electronic structure in a heterogeneous glass as well as beam-induced oxidation.

The interpretation of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios derived from spectroscopic data in silicate glasses requires particular caution. Previous studies have shown that, at ambient conditions, $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios can remain constant even as coordination environments and clustering behavior evolve [197, 198]. In addition, XANES-based calibrations for haplobasaltic glasses emphasize that changes in spectral features may reflect variations in coordination and local structure rather than purely redox-driven transformations [199].

6.5.3 Spin-state evolution from SMS

SMS results show a decoupled response of Fe^{2+} and Fe^{3+} . Fe^{2+} might respond primarily through structural reorganization of its local environment while remaining largely HS over the investigated pressure range. In contrast, Fe^{3+} shows less evidence for major coordination changes but contributes more significantly to the gradual spin reduction. The isomer shift values for Fe^{2+} fall entirely within the HS region across all pressures, indicating that Fe^{2+} remains in a HS state up to at least 100 GPa. In contrast, the corresponding values for Fe^{3+} lie near the boundary between HS and LS regimes, suggesting the onset of a gradual spin transition. However, the overlap of spin-state fields and the inherent uncertainties of Mössbauer-based assignments in disordered systems prevent a definitive identification of a complete spin crossover for Fe^{3+} .

Such behavior is expected for disordered systems such as glasses. In contrast to crystalline materials, where spin transitions can occur over relatively narrow pressure intervals, glasses contain a distribution of local environments with varying bond lengths and distortions. This leads to a broad and continuous spin crossover distributed over a wide pressure range [190]. The results here presented contribute to the finding on Gu et al. [192], describing a gradual spin transition without a full spin crossover to LS state and to Solomatova et al. [194], where they expect Fe^{2+} does not change the spin-state up to 120 GPa.

6.5.4 Implications for melts and deep-mantle iron behavior

The present results provide insight into the behavior of iron in silicate systems at high pressure, with implications for melts in the deep Earth. The distinct responses of Fe^{2+} and Fe^{3+} to compression suggest that structural and electronic properties of iron-bearing melts are strongly influenced by both valence state and local coordination environment [1, 190, 193].

The partitioning of iron between coexisting phases depends sensitively on its oxidation state, coordination number, and spin-state. Because Fe^{2+} and Fe^{3+} differ in ionic radius and structural role, pressure-induced changes in coordination and spin-state can modify

their relative stability in melts and crystalline phases [1, 218]. The presence of mixed-valence states, such as $\text{Fe}^{2.5+}$, can further complicate this behavior by introducing partial electron delocalization in disordered systems [99].

At the same time, caution is required when extrapolating results from cold-compressed glasses to high-temperature melts. Glasses are metastable and kinetically arrested, and their local structures may not fully equilibrate under compression [208]. Experimental studies of dynamically compressed silicate melts have shown that iron can become predominantly LS at extreme pressure-temperature conditions, whereas glass studies generally indicate broader and more persistent HS or mixed-spin behavior over comparable pressure ranges [57, 190, 192, 193].

This difference suggests that the spin-state of Fe in glasses may underestimate the degree of spin collapse in coexisting melts at deep-mantle conditions. Consequently, glass-based measurements should be complemented by high-temperature studies when addressing geophysical applications [57, 208].

The observed pressure-dependent changes in coordination and spin-state are also expected to influence element partitioning between melts and coexisting crystalline phases. Partition coefficients of iron depend sensitively on oxidation state, site geometry, and electronic configuration, all of which are modified under compression [1, 5, 190]. In particular, the structural adaptability of Fe^{2+} and the gradual spin-state reduction of Fe^{3+} may lead to changes in effective ionic size and bonding behavior, thereby affecting the relative stability of iron in different phases [1, 57].

Furthermore, the presence of mixed-valence states in disordered systems may blur the distinction between Fe^{2+} and Fe^{3+} endmembers, introducing additional complexity into partitioning behavior. As a result, iron partitioning at high pressure is likely governed by a combination of valence state, local structure, and electronic configuration, rather than by oxidation state alone [99, 197, 198, 208].

Ferrous iron shares the same charge as Mg^{2+} and exchanges with it between coexisting phases through Fe-Mg exchange reactions [188]. High-pressure studies of silicate glasses show that Fe^{2+} undergoes significant changes in coordination environment and local structure with increasing pressure [194, 217]. Because partitioning behavior depends on the electronic and structural state of iron, including its spin and valence [188], these structural changes may influence the relative stability of Fe^{2+} compared to Mg^{2+} and thereby affect Fe-Mg partitioning.

Similarly, ferric iron competes with Al^{3+} for network-forming positions in silicate structures. The relative structural stability of Fe^{3+} observed in this study, combined with its contribution to spin-state changes, indicates that Fe^{3+} may increasingly behave as a network-modifying cation at high pressure. This may influence the distribution of Al and Fe^{3+} between coexisting phases and affect the degree of polymerization in silicate melts. In Al-bearing systems, ferric iron is preferentially incorporated into the silicate phase through coupled substitution mechanisms involving Al^{3+} , such as $\text{Fe}^{2+} + \text{Si}^{4+} = \text{Fe}^{3+} + \text{Al}^{3+}$ [188]. Consequently, variations in Fe^{3+} concentration are closely linked to both aluminum content and pressure-induced changes in spin and valence states, which together influence iron partitioning between coexisting phases. Changes in $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios may therefore indirectly affect the structural role of iron and the distribution of network-forming cations in silicate systems.

Because spin transitions modify the effective ionic radius of iron, they can influence its partitioning behavior under deep-mantle conditions [1]. In particular, the gradual reduction in spin-state inferred from XES suggests that iron may become progressively more compatible in dense phases at high pressure, although this effect is best constrained in high-temperature experiments on silicate melts [57].

These structural and electronic changes may also affect macroscopic melt properties. Variations in iron coordination and spin-state can influence melt density, compressibility, and potentially viscosity, thereby modifying melt mobility and segregation behavior in the deep mantle [1]. In addition, changes in the relative abundance of Fe^{3+} may influence melt structure and polymerization, although this effect remains difficult to quantify in disordered systems under high pressure [20].

6.5.5 Conclusion

In summary, based on HBG 1, it exhibit a coupled structural and electronic response to compression that depends strongly on iron valence state. Fe^{2+} undergoes significant modifications of its local coordination environment, while Fe^{3+} remains comparatively stable in its structural role but contributes more strongly to the observed decrease in average spin-state. The apparent increase in $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ in the more reduced samples HBG 2 and HBG 3 is likely influenced by a combination of pressure-induced site redistribution or beam induced oxidation.

The most consistent interpretation is that compression drives a redistribution of Fe^{2+} environments toward more distorted or higher-coordinated configurations, while Fe^{3+} contributes more strongly to the gradual spin-state reduction.

7 Summary and outlook

This study investigates the structural and electronic behavior of iron under high-pressure conditions relevant to the Earth's lower mantle by combining results from experiments on Fe_2O_3 and iron-bearing haplobasaltic glasses. By linking simplified oxide systems with silicate melts, the work provides complementary constraints on how iron responds to compression in different chemical environments, with a particular focus on the interplay between valence state, spin-state, and local structure.

For Fe_2O_3 , *in situ* laser-heated XES and temperature-quenched RXES and XRD were combined to investigate the coupled electronic and structural evolution under HP and HT conditions. The results demonstrate that spin-state, crystal structure, and phase stability evolve in a strongly interdependent manner along the Earth's geotherm.

At pressures around 38 GPa, Fe_2O_3 remains in a HS configuration despite partial structural transformation from the hematite ($\alpha\text{-Fe}_2\text{O}_3$) to the $\iota\text{-Fe}_2\text{O}_3$ structure. This observation indicates that crystallographic transitions alone do not necessarily induce changes in electronic state and that structural and electronic degrees of freedom may remain partially decoupled within the HS regime.

At intermediate pressures near 64 GPa, Fe_2O_3 enters an extended mixed-spin regime characterized by changes in XES spectral features and intermediate spin values. This behavior reflects a spin crossover from HS to LS state on specific sites. Instead, it is associated with pressure induced structural changes and with HT the formation of mixed-valence iron oxides, particularly Fe_5O_7 . The coexistence of HS Fe^{2+} and LS Fe^{3+} within these phases contributes significantly to the observed spectroscopic response, demonstrating that the apparent spin-state is governed by the evolving phase assemblage and its coordination topology.

At pressures of approximately 80 GPa, Fe_2O_3 exhibits a predominantly LS state under cold compression. Upon heating an increased HS contribution is observed, followed by partial relaxation after quenching. This behavior coincides with extensive phase transformations and the stabilization of $\text{Fe}_{25}\text{O}_{32}$ as a dominant quenched phase, which was previously known to be synthesized from Fe_3O_4 . At these conditions, the electronic response reflects the balance between LS ferric phases and HS ferrous components within complex, mixed-valence assemblages.

Overall, the Fe_2O_3 results demonstrate that electronic transitions in iron oxides cannot be interpreted independently of structural transformations and phase relations. Instead, spin-state evolution is closely linked to changes in coordination environment, crystal symmetry, and chemical composition, particularly under HT conditions where phase transformation becomes relevant.

Complementary insights are obtained from Fe-bearing haplobasaltic glasses, which provide a simplified model system for silicate melts. In these materials, iron exhibits a coupled structural and electronic response to compression that depends strongly on its

valence state. Ferrous iron shows significant changes in local coordination, consistent with increasing distortion or coordination number under pressure. In contrast, ferric iron remains comparatively stable in its structural role but contributes more strongly to the observed decrease in average spin-state.

The evolution of spin-state in the glasses is gradual and incomplete, reflecting the distribution of local environments inherent to disordered systems. The data indicates that compression leads to a redistribution of Fe^{2+} environments toward more distorted configurations with electron delocalization, while Fe^{3+} may show a slight decrease in spin. The apparent increase in $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ observed in more reduced samples can be explained by local structural and electronic effects as well as beam induced oxidation.

These results highlight the importance of considering both structural disorder and mixed valence when interpreting spectroscopic signatures in silicate glasses. They further demonstrate that integrated approaches combining multiple techniques are essential for reliably constraining iron behavior under high-pressure conditions.

By combining observations from Fe_2O_3 and haplobasaltic glasses, this study shows that the response of iron to lower mantle conditions is governed by a complex interplay between electronic state, local structure, and phase assemblage. In crystalline oxides, this interplay is expressed through phase transitions and the formation of mixed-valence compounds, whereas in silicate glasses it manifests as a continuous redistribution of local environments within a structurally disordered network.

Together, these results demonstrate that the spin-state evolution of iron at lower mantle conditions is controlled by the evolving structural and chemical environment. In Fe_2O_3 , the observed electronic behavior reflects phase transformations and the formation of mixed-valence oxide assemblages in the mixed-spin regime, whereas in haplobasaltic glasses it arises from a continuous redistribution of local coordination environments within a disordered network. This implies that electronic transitions in iron are intrinsically linked to redox processes and phase properties in the deep mantle, and therefore directly affect the density, structure, and mobility of iron-bearing melts and solids. Consequently, variations in iron speciation may play an active role in controlling melt generation, transport, and chemical differentiation in Earth's lower mantle. In the lower mantle, the behavior of iron is not defined by pressure itself, but by how pressure reshapes its structural, electronic, and redox environment.

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During the preparation of this thesis, ChatGPT and Perplexity were used to assist with linguistic revision, phrasing, and clarity. The scientific content, interpretation, and conclusions were developed independently by the author, who bears full responsibility for the content of this thesis.

A Appendix

A.1 DAC preparation

Here, detailed instructions for cell preparation with alignment, gluing, gasket making and gas loading is given. The instructions are made for the preparation of a BX90-RD cell using one ST and a BA or MD as a counterpart. Required materials:

- 1 cell (BX90-RD)
- diamond mounting jig
- 2 diamonds (1 ST and 1 BA or MD)
- 2 diamond seats (specific for the diamonds used)
- adhesive (Henkel Loctite EA 9514 also known as Hysol 9514)
- rhenium gasket (200–250 μm thickness)
- 2-propanol
- tweezers, syringe needle, tungsten needle, cotton swabs or Q-tips
- 'Blu Tack'
- binocular microscope and oven

Very important is thorough cleaning during all steps. In this thesis mainly 2-propanol was used since acetone seems to have an effect on the adhesive. Nearly all steps are done under the binocular microscope to guarantee the best cleaning results. Further, the adhesive is best stored airtight in a refrigerator.

A.1.1 Alignment and gluing

Here a detailed step to step guide is given for diamond and seat alignment as well as gluing the diamonds onto the seats. For the first part the diamond mounting jig (short: jig) is used for gluing the ST onto its seat.

1. Preheat the oven to 180°C
2. Clean the jig using isopropanol with cotton swaps.
3. Clean the standard seat, especially the underside, and place it in the center of the jig cylinder. Tip: Count the turns of the set screws under the binocular microscope or measure the distance from the flattened side of the seat to the beginning of the holder.
4. Clean the seat thoroughly again and set the jig aside
5. Clean the ST, also paying attention to the underside to ensure there will be no dirt causing stress at pressure.
6. Place the ST on the seat inside the jig. Center the ST as good as possible while ensuring it is leveled.

7. The upper part of the jig with the tip is inserted into the jig, holding the ST in place. It should fit perfectly, otherwise adjustment of the seat with the alignment screws is necessary.
8. For the fine adjustment of the seat, so that the standard diamond is centered on the seat while using the binocular microscopes scale: It is best to take the straight edge of the diamond and count the markings of the scale until the seat slopes down at the side; this should be fairly even on all sides. Subsequently, the jigs screws can be hand tightened for locking the diamond in place. Tip: use a large magnification for best precision.
9. If the alignment is satisfactory, proceed to gluing. A small syringe needle proved to be very handy for picking up adhesive and transfer it onto the edge of the diamond and seat. Therefore, the jig is best placed on its side. The adhesive has to be all around the diamond and not too sparse. It should neither touch the top part of the jig nor should it get onto the culet. Although, adhesive on the pavilion surface is desirable.
10. Place the jig into the oven and leave it there for at least 30 Minutes, better 60 Minutes for solidifying the adhesive.
11. When the jig is cooled down, check that there is not too much adhesive on the diamonds surface. If necessary, scrape it off with a syringe needle or scalpel.

After cooling down of the jig, the diamond anvil cell itself is required:

12. The seat with the diamond is placed in the outer cylinder of the DAC and aligned centrally utilizing the scale of binocular microscope. Count the markings of the scale for measuring the distances and find the exact center. The alignment screws for fixing the seat help to find the right position, but must be tightened carefully, as tightening can quickly cause the seat to shift.

Now, the BA or MD follows:

1. the BA or MD seat is placed into the piston and is centrally aligned. Here as well the markings of the binocular microscope are used to determine the middle. The alignment screws can help to push the seat into the right position, but here too, tightening can quickly cause the seat to shift. Hereinafter, bring the cylinder and piston together and nearly close it to check positioning of the seat.
2. Once this has been done, the BA/MD can be placed onto the seat (after everything is spotless), but not yet glued. Tread carefully, since the diamond can fall out, so never hold it upside down.
3. Insert the piston into the cell and bring the diamonds very close together, but without them touching. Tip: the safety screws on the cylinder part can help to ensure, not too much pressure is applied when pressing by hand. This can prevent the collision of the diamonds and their breaking.
4. Afterwards, carefully turn the DAC onto its side and bring the piston and cylinder and therefore the diamonds together with a distance left of around 5 μm .
5. Then, turn the cell again, so the BA/MD is on the bottom and the horizontal alignment follows.
6. First, try to align both diamond culets exactly on top of each other by pushing with the alignment screws of the BA/MD seat if necessary and tighten them if satisfactory.

7. For the tilt-alignment, the two diamonds are brought together until they are almost touching, but very carefully and tentatively. The second (still loose) diamond is then gently nudged into place. Newton's fringes will be visible through the binoculars as soon as the culet surfaces are in contact. The more of these fringes are visible, the poorer the alignment. The goal is to achieve a maximum of two orders of fringes. The "nudging" is continued until the fringes disappear as much as possible.
8. Then the glued ST diamond can be brought completely onto the loose BA/MD diamond so that it is supported and held in position. The Newton fringes slowly disappear.
9. Then you have to be extremely careful not to move the cell jerkily, otherwise the diamonds will break. Now the adhesive can be applied to the BA/MD using a syringe needle or similar, so that the adhesive holds the diamond in place.
10. Screw in a safety screw from below so that the culet surfaces slowly separate from each other again and are sufficiently spaced apart. This is because they must not touch each other in the oven during heating.
11. Place the cell in the oven and allow hardening at 180°C for about an hour.

The next process is called pre-indentation and is of importance, since the heating can cause a shift in alignment.

1. First, clean the area.
2. Take a piece of gasket (it can be old or used, but use a new section) and place it on the BA/MD with a little 'Blu Tack' and push the piston into the cylinder.
3. Press until about half of the pavilion surfaces are touching the gasket. Where it touches, the rhenium gets significantly darker there.
4. Open it up and measure the indentation with a point micrometer; it should be about 100 μm with a 200 μm gasket.
5. Clean again.
6. Place them close together without touching.
7. Check whether the horizontal alignment still fits, otherwise adjust and repeat until it is OK after pressing forward. Tip: Sometimes it can also help to shift "over" in the other direction if it keeps pushing back.
8. Clean again.
9. Bring the diamonds together (use safety screw if wanted) and check the number of Newton fringes. Tip: More than four orders are definitely not good, a maximum of one to two orders can be tolerated depending on the pressure the diamonds are planned to withstand. A pleasing alignment shows only a slight green and at maximum a light red shimmer across the entire culet.

A.1.2 Gasket and sample loading

Preparing the Gasket involves the indentation process and drilling a hole. A step-by-step guide is given for indentation, hole drilling and handling the electric discharge drilling machine (EDM) in Potsdam at the Lab from Prof. Dr. Max Wilke. At last, the process of sample loading is explained as well. Starting with the indentation:

1. Pre-indent to 40-50 μm , verify with a point-micrometer.

2. Flip the gasket 180°.
3. Indent again to 20-25 μm . Tip: Prefer a bit over 25 μm in comparison to under 20 μm .
4. Place in the EDM and measure the depths in the center of the culet and then on the outside at four points around the edge. Note all values displayed by the EDM.
5. Measure the width of the hole (half culet size + pavilion area) under the binocular microscopes. (In Potsdam, the old binocular microscope, with the scale in the eyepiece, has a chart behind them on the wall with lengths for estimation.)
6. Calculate the angle ($\arctan(\text{hole depth}/(0.5 \cdot \text{hole width}))$). If the angle is less than 20°, it is good for usage. Tip: if the angle is slightly higher, one can grind down a bit of the gasket and check the measurement with the EDM and binocular microscope again to calculate the angle once more. This eventually prevents the necessity to redo the whole process. Tip: grinding in general removes a 'wall' which can be a result from indenting, and this wall prevents a good emission through the side. Therefore, grinding is always advised.

Before the drilling of the hole is described, a short manual for handling the EDM (based in Potsdam) is given:

1. Turn on the light, by using the knob behind the gray metal box at the top.
2. Take the gray metal piece with the dark gray basket and place the gasket under the gold/brass-colored plate, centering it as much as possible and securing it loosely with the screws.
3. Then take the entire bracket and slide it into the two black posts, but do so slowly and carefully, as you are sliding it toward the needle, which is very sensitive. Get it close to the needle without touching it and secure it to the black post on one side with a screw.
4. At the back, attach the wire to the pole on the dark gray gasket bracket.
5. Take a look at the gasket indentation, or better still, the needle with the microscope. This has 3 degrees of freedom. Top right and left = focus in both directions. Bottom front = front/back. Bottom right and left = move right/left depending on the direction of rotation.
6. Set the switch on the controller to 'on'.
7. The other switches should be set to 'High' and 'Tool', then set the red switch to 'down'.
8. Then press R/S and the needle will move down until it touches the gasket and stops automatically on contact. Tip: For taking it slowly, press 'R/S' again to stop it.
9. For moving the gasket indentation towards the needle, use the gray adjusting screws/micrometer screws on the dark gray box.

Finally, for drilling the hole itself:

1. Take the desired needle size. Tip: 80 μm for 200 μm culet, 60 μm for 150 μm culet and 40 μm for 120 μm culet. It should be roughly around 30 to 50% of the culet size.
2. Needle change: Take the box with all the needles and open it. Take the tweezers with the rubber ends and hold the needle at the top. Take the white rod to loosen the golden lower screw of the needle holder and replace the needle. Repeat and important: Place a note on top of the gray box with the current needle diameter.

3. Move the needle to the center of the culet and place it on top.
4. For checking the center, use the black rods at the very outside and turn them 45° in both directions. Then adjust the focus of the microscope again. If it does not fit, raise the needle! And slide the gasket to fit using the micrometer screws. Then check all directions again. It is best to leave the needle down for checking, but never move the gasket when the needle is down.
5. When satisfied with alignment, switch from 'Tool' to 'Limit'.
6. Calculate the value displayed on the EDM, e.g., 0.542 plus 50 microns, i.e., 0.592, and set the value using the wheel on the far right.
7. Switch back from 'Limit' to 'Tool'.
8. The values on the grey box should be set to '2' *upmu*J discharge energy and 0.2 W peak power. The polarity switch should be set to 'normal'.
9. Add turpentine substitute in the glass ampule to the gasket/needle using a pipette.
10. Set the red switch to 'Mach' and press 'R/S'.
11. The hole is drilled automatically and the needle stops automatically after the previously set +50 μm .
12. Then set the red switch to 'up' and raise the needle a good distance.
13. Now the holder can be loosened and the gasket removed.
14. Clean the gasket holder with a cloth and wipe off any remaining turpentine substitute.
15. Now place the gasket in an ultrasonic bath in ethanol or similar for 2 minutes.
16. Examine the hole from both sides under a microscope.

In case, there is not the right sized needle already in the holder or the needle is broken, here are the steps to attach a new needle to the holder. In the following needle and wire can be used interchangeably, since the nice is a wire in principle.

1. First, find a suitable wire in diameter.
2. Remove the old wire/needle from the holder with acetone/isopropyl alcohol, etc., possibly also in an ultrasonic bath. The previous needle can then be thrown away.
3. Above the EDM is a box with a black bottom and a transparent lid. Inside is a box with transparent vials and black lids. These contain pieces of wire in various sizes. Use a toothpick moistened with alcohol to remove one of these pieces.
4. To ensure that the wire is straight, take the two glass plates, also from the box, place them between the wire and roll it gently over them.
5. Clean the needle holder again with a Q-tip after the ultrasonic bath.
6. Then take the moistened toothpick and apply saliva to the needle holder. Then take the wire and place it in the pre-milled holder and align it very straight.
7. Take the silver paste out of the box, shake it well, and then wipe it down the holder so that the liquid moves over the needle. Do this on both sides so that the needle is covered with silver.
8. Then you can wait or place the whole thing on the heating plate at about 70° for about 2 minutes.
9. Insert the needle into the EDM and set the switch at the front from 'normal' to 'reverse'. Take an old gasket and place it underneath at any point.
10. Note the value displayed when the needle touches the gasket.
11. Use turpentine substitute again here.
12. Then use reverse mode to move around the value 100 and then stop; this will make the wire look nicer. Set back to 'normal'.

When the gasket is indented and the hole drilled, it is ready for usage. Thus, the next steps explain how to load the sample into the gasket hole:

1. Clean everything thoroughly, placing the gasket in an ultrasonic bath again if necessary.
2. Place the gasket on the MD and close the cell. Press down slightly, but not too hard, just enough so that the gasket touches the ST. Take everything apart again and check that there are no rhenium residues on the MD or ST. If there are, clean everything and repeat until there are no more residues on the culets. Tip: for removing residue sandpaper is the easiest and most effective option.
3. Then close it again and open it again so that the gasket fits properly on the MD.
4. Take a sample and place it in the center of the culet of the ST. Not too much sample, but also not too little. It should not fill the entire hole when gas is loaded. Tip: For a 60 μm hole, around 30 μm sample in the middle.
5. When there is no gas loading, for example for glasses: take the powdered glass and press it into the hole on the MD several times, closing it again and again until it is full. (For powdering glass: a very small piece of maximum 20 μm is placed in a small mortar and mixed with isopropanol against dust. Each grain should be not bigger than 0.5 μm)
6. Then leave the ST at the bottom and close the cell with the MD from above. Bring them together slowly and check whether the sample is in the center of the hole. Don't close it completely, just close the cell slowly.
7. If the sample is not centered, open the cell again and repeat until it is centrally placed.
8. Once the position is correct, close the cell once. Do not apply too much pressure, otherwise the hole may shrink, which means it was tightened too much.

Now the cell can be prepared for the gas loading process, which is described in the following section.

9. Remove the screw(s) and turn the cell over.
10. Then carefully screw in a safety screw from the back and observe through the binoculars. As soon as there is a change in the shimmer of the gasket, the cell is open again and ready to be loaded with gas. Tip: If the whole hole is filled with sample, one will know if there is enough sample in it, if the hole does not shrink at higher pressure. Further, the cell does not have to be opened up again, because the step of gas loading is not required.
11. Carefully screw the screws in with washers on them, but only loosely, without tightening them.

A.1.3 Gas loading

The gas loading was done at the GFZ in Potsdam and the handling was done by Prof. Dr. Max Wilke. But here are some valuable information about handling gas loading:

1. Place the DAC into the holder.
2. Before applying 2000 bar, write down the numbers on the display as a reference.
3. Pressurize up until 2000 bar.

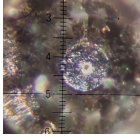
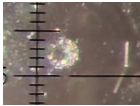
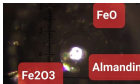
4. Close the DAC: reach +550 during closing, if the starting value was -50. (a total of +600 compared to the starting number)
5. When releasing the pressure, hold back the closing until the value rises to 700 (i.e. +150 in relation).
6. When tightening the screws by: -15 from the value for 700 (from 700 to 685). Then there is with 5 pairs of washers nearly no pressure on the cell, but it is closed. So maybe going to a value to -30 (from 700 to 670) is also sufficient.

Afterwards the pressure can be checked with optical Raman spectroscopy. This procedure is explained in 4.1.3.

A.2 List of used diamond configurations and cells

Here, an overview of all cells with the diamond configurations, their culet sizes, gasket hole sizes, starting and ending pressure is provided. There were three different beamtimes for the two topics in this thesis. For the Fe_2O_3 in November 2022 at P01, DESY an overview is in table A.1.

Table A.1: Overview of diamonds and cells for the Fe_2O_3 experiment at P01, PETRA III, DESY in November 2022.

Pic.	CN ^a	D1 ^b	D2 ^c	CD ^d	PM ^e	HD ^f	SP ^g	EP ^h	Note ⁱ
	22D01	ST	MD	200	Argon	80	14	MD broke	D33 1, D32 1
	19C02	ST	MD	200	Argon	80	9	38	D33 2, D32 2
	22D02	ST	MD	200	Argon	80	64	64	3 samples
	22D03	ST	MD	150	Argon	65	10	80	

^a cell name

^b first diamond

^c second diamond

^d culet diameter [μm]

^e pressure medium

^f hole diameter [μm]

^g starting pressure [GPa]

^h ending pressure [GPa]

ⁱ special feature / inventory no.

Regarding the topic of HBG, the first beamtime in June 2022 at the ESRF ID20 and ID18 the configurations are shown in table A.2 and for the second beamtime at ID20 at the ESRF in April 2023 the information is in table A.3.

Table A.2: Overview of diamonds and cells used in the first HBG experiment at ID20 and ID18 in June 2022.

SN ^a	CN ^b	D1 ^c	D2 ^d	CD ^e	PM ^f	HD ^g	SP ^h	EP ⁱ	Note ^j
HBG 1 61% Fe ³⁺	RD02	ST	MD	120	x	40	0.21	120	D35 1, D34 1
HBG 2 47% Fe ³⁺	21N03	ST	MD	120	x	40	1.15	118	D35 3, D34 3
HBG 3 13% Fe ³⁺	19C02	ST	MD	120	x	40	0.4	118	D35 2, D34 2

^a sample name^b cell name^c first diamond^d second diamond^e culet diameter [μm]^f pressure medium^g hole diameter [μm]^h starting pressure [GPa]ⁱ ending pressure [GPa]^j special feature / inventory no.**Table A.3:** Overview of diamonds and cells used in the second HBG experiment at ID20 in April 2023.

SN ^a	CN ^b	D1 ^c	D2 ^d	CD ^e	PM ^f	HD ^g	SP ^h	EP ⁱ	Note ^j
HBG 1 61% Fe ³⁺	21N05	ST	MD	120	x	40	7	81	D41 3, D40 3
HBG 3 13% Fe ³⁺	21N03	ST	MD	120	x	55	21	65	D41 2, D41 1
HBG 3 13% Fe ³⁺	22D01	ST	MD	120	x	40	8	116	MD D40 1
Fe ²⁺ Reference	22D03	ST	MD	120	x	40	12	115	after XES 46
Fe ³⁺ Reference	Rd02	ST	BA	150	x	40	8	118	D29 2, D28 2
ambient cell	19C02	ST	MD	200	x	x	x	x	x

^a sample name^b cell name^c first diamond^d second diamond^e culet diameter [μm]^f pressure medium^g hole diameter [μm]^h starting pressure [GPa]ⁱ ending pressure [GPa]^j special feature / inventory no.

A.3 Full EPMA analysis result on HBG samples

Full EMPA analysis results from Prof. Dr. Harald Behrens of Leibniz University of Hanover on the 3 HBG compositions with their corresponding average for their elemental distribution.

Glass 1 with 61% Fe³⁺/Fe_{tot} (production name HB_JFe57) is in table A.4.

Glass 2 with 47% Fe³⁺/Fe_{tot} (production name HB_JFe57_3CO2) is in table A.5.

Glass 3 with 13% Fe³⁺/Fe_{tot} (production name HB_JFe57_2) is in table A.6.

Table A.4: EMPA analysis results of Glass 1 detailing the elemental distribution (in wt%).

measurement	Na ₂ O	MgO	TiO ₂	FeO	K ₂ O	SiO ₂	Al ₂ O ₃	MnO	CaO	Total
1	0.148	6.445	0.214	6.552	0.071	45.322	23.980	0.000	17.171	99.903
2	0.183	7.047	0.140	6.838	0.087	45.691	23.931	0.004	17.031	100.952
3	0.040	6.580	0.136	6.780	0.081	46.278	24.318	0.013	17.114	101.340
4	0.144	6.471	0.185	6.682	0.076	45.342	25.229	0.000	16.908	101.037
5	0.000	6.637	0.163	6.947	0.066	42.650	27.806	0.029	17.004	101.302
6	0.086	6.762	0.172	6.681	0.087	44.552	25.769	0.022	16.871	101.002
7	0.010	6.516	0.199	6.834	0.050	44.763	25.131	0.000	16.640	100.143
8	0.000	6.365	0.147	6.951	0.053	42.496	28.511	0.000	16.612	101.135
9	0.111	6.735	0.091	6.730	0.097	44.790	25.683	0.000	16.606	100.843
10	0.158	6.721	0.146	6.567	0.060	44.799	25.508	0.014	16.855	100.828
11	0.057	6.741	0.219	6.636	0.090	43.717	25.626	0.000	16.887	99.973
12	0.114	6.596	0.226	6.314	0.095	44.839	25.890	0.005	16.874	100.953
13	0.148	6.712	0.000	7.411	0.081	44.839	24.682	0.000	16.699	100.572
14	0.129	6.829	0.089	6.689	0.042	42.878	27.465	0.001	16.577	100.699
15	0.000	6.750	0.154	6.477	0.089	43.215	28.363	0.018	16.555	101.621
16	0.197	6.293	0.183	6.631	0.097	43.601	27.182	0.000	16.833	101.017
17	0.032	6.630	0.179	6.316	0.042	44.578	26.188	0.011	16.224	100.200
18	0.042	6.429	0.158	6.420	0.102	43.800	27.946	0.000	16.436	101.333
19	0.128	6.543	0.170	6.667	0.082	44.183	27.220	0.006	16.465	101.464
20	0.039	6.451	0.099	6.205	0.063	44.564	27.383	0.002	16.432	101.238
21	0.097	6.882	0.119	6.782	0.101	44.395	26.660	0.015	16.370	101.421
22	0.031	6.701	0.130	6.112	0.078	42.067	29.436	0.012	16.451	101.018
23	0.056	6.423	0.234	6.302	0.108	44.604	26.485	0.000	16.394	100.606
24	0.000	6.684	0.240	7.138	0.058	44.940	26.309	0.000	16.441	101.810
25	0.075	6.417	0.112	7.474	0.059	43.808	27.148	0.023	16.431	101.547
26	0.014	6.700	0.098	7.145	0.081	43.106	26.641	0.025	16.717	100.527
27	0.075	6.742	0.159	6.911	0.121	44.351	26.587	0.000	16.857	101.803
28	0.023	6.847	0.108	6.765	0.073	44.766	27.107	0.001	16.528	102.218
29	0.000	6.721	0.200	6.705	0.061	44.686	25.673	0.011	16.779	100.836
30	0.014	6.440	0.139	6.979	0.013	44.065	25.580	0.012	16.172	99.414
31	0.107	6.819	0.249	6.794	0.107	44.831	25.323	0.018	16.621	100.869
32	0.050	6.537	0.174	6.967	0.088	44.716	26.669	0.014	16.398	101.613
33	0.079	6.559	0.225	6.372	0.059	44.480	26.671	0.017	16.237	100.699
34	0.015	6.311	0.186	6.405	0.091	44.477	26.683	0.000	16.349	100.517
Average	0.071	6.619	0.160	6.711	0.077	44.300	26.376	0.008	16.634	100.955

Table A.5: EMPA analysis results of Glass 2 detailing the elemental distribution (in wt%).

measurement	Na ₂ O	MgO	TiO ₂	FeO	K ₂ O	SiO ₂	Al ₂ O ₂	MnO	CaO	Total
1	0.054	6.609	0.244	6.972	0.006	44.715	23.896	0.017	17.539	100.052
2	0.000	6.849	0.078	7.089	0.006	45.487	23.561	0.000	17.120	100.190
3	0.001	6.688	0.284	6.666	0.005	45.493	23.425	0.002	17.513	100.077
4	0.000	6.975	0.199	7.020	0.027	46.106	24.099	0.000	17.313	101.739
5	0.162	6.630	0.147	6.787	0.029	45.492	23.821	0.003	17.360	100.431
6	0.054	6.904	0.244	6.775	0.018	45.115	23.660	0.010	17.414	100.194
7	0.095	7.028	0.146	6.900	0.025	45.551	23.562	0.000	17.314	100.621
8	0.142	6.727	0.112	7.401	0.002	45.768	23.358	0.013	17.618	101.141
9	0.061	7.089	0.175	6.937	0.027	45.817	23.636	0.000	17.228	100.970
10	0.119	6.537	0.157	6.829	0.012	45.045	22.899	0.025	17.376	98.999
11	0.087	6.904	0.093	7.051	0.026	45.036	23.613	0.035	17.436	100.281
12	0.017	6.757	0.177	6.589	0.022	45.261	23.397	0.000	17.377	99.597
13	0.000	6.933	0.245	6.717	0.007	45.910	23.621	0.013	17.544	100.990
14	0.029	7.000	0.163	7.125	0.011	45.862	23.363	0.000	17.467	101.020
15	0.181	6.927	0.150	6.985	0.027	45.624	23.730	0.000	17.433	101.057
16	0.050	6.595	0.090	6.816	0.026	45.898	23.531	0.000	17.380	100.386
17	0.087	6.764	0.077	6.727	0.015	45.994	23.933	0.007	17.572	101.176
18	0.029	6.842	0.192	6.864	0.010	45.748	23.597	0.000	17.380	100.662
Average	0.065	6.820	0.165	6.903	0.017	45.551	23.595	0.007	17.410	100.532

Table A.6: EMPA analysis results of Glass 3 detailing the elemental distribution (in wt%).

measurement	Na ₂ O	MgO	TiO ₂	FeO	K ₂ O	SiO ₂	Al ₂ O ₃	MnO	CaO	Total
1	0.083	6.751	0.303	6.421	0.114	46.771	23.717	0.000	17.276	101.436
2	0.151	6.520	0.174	6.817	0.086	46.314	23.834	0.014	17.399	101.309
3	0.097	7.003	0.144	6.250	0.098	46.134	24.118	0.025	17.435	101.304
4	0.171	6.961	0.081	6.561	0.091	46.824	23.921	0.000	17.074	101.684
5	0.060	6.889	0.131	6.181	0.120	46.403	23.772	0.000	17.333	100.889
6	0.071	6.811	0.154	6.245	0.128	46.164	23.781	0.022	17.133	100.509
7	0.058	6.887	0.234	6.488	0.092	46.250	23.588	0.000	17.139	100.736
8	0.093	6.729	0.079	6.194	0.069	46.579	24.379	0.010	17.648	101.780
9	0.035	6.600	0.129	6.640	0.050	45.803	23.972	0.011	17.575	100.815
10	0.103	7.022	0.105	5.857	0.080	46.339	24.190	0.000	17.047	100.743
11	0.068	6.719	0.155	6.280	0.082	45.973	23.827	0.000	17.261	100.365
12	0.212	7.001	0.122	6.488	0.110	46.405	24.469	0.013	17.441	102.261
13	0.049	6.981	0.094	6.497	0.059	45.421	23.895	0.007	17.310	100.313
14	0.014	6.949	0.151	6.627	0.091	46.317	23.793	0.001	17.560	101.503
15	0.146	6.623	0.188	6.150	0.114	45.981	24.001	0.000	17.477	100.680
16	0.096	7.134	0.089	6.234	0.081	46.361	24.056	0.004	17.516	101.571
17	0.115	6.955	0.146	6.536	0.097	46.611	24.299	0.000	17.167	101.926
18	0.067	6.983	0.191	5.754	0.096	46.577	23.850	0.005	17.152	100.675
19	0.111	6.867	0.191	6.548	0.078	45.681	24.470	0.000	17.565	101.511
20	0.014	6.666	0.151	6.469	0.102	45.680	24.023	0.000	17.509	100.614
21	0.075	7.158	0.123	6.361	0.074	46.373	23.778	0.000	17.256	101.198
22	0.000	6.684	0.334	6.218	0.042	46.141	24.123	0.009	17.316	100.867
23	0.154	6.825	0.252	6.380	0.107	46.428	24.348	0.017	17.266	101.777
24	0.204	6.716	0.076	6.190	0.127	46.059	24.017	0.000	17.359	100.748
25	0.124	6.810	0.266	6.330	0.087	45.712	24.251	0.000	17.292	100.872
26	0.103	6.629	0.129	6.273	0.107	46.260	24.073	0.005	17.498	101.077
Average	0.095	6.841	0.161	6.346	0.092	46.214	24.021	0.006	17.346	101.122

A.4 Instructions on how to use Standa controller for von Hámos and focussing crystals

The Standa controller operates the motors necessary for adjusting the detector and von Hámos spectrometer height as well as the individual motors for crystal movement. Here an in depth description including wiring is given.

Hardware

For operating the individual motors of the crystals at the von Hámos, the spectrometer has a motor-box (cf. Fig. A.1 left) which needs to be wired with the Standa controller (cf. Fig. A.1 right). Special attention is needed, that the cables are connected to the same motors between motor-box and Standa controller.



Figure A.1: left) Motor-box of the von Hámos spectrometer for moving the individual motors for the crystals. right) Standa controller for controlling the motor movement of the crystal motors. top front view bottom backside view.

For moving the spectrometer itself in height as well as the detector, the cables of their motors need to be connected to the patch-box (cf. Fig. A.2 top). Further, one cable need to connect the patch-box to the Standa controller (cf. Fig. A.2 bottom). The cable can either be same as used before for moving the crystal motors, by removing one cable from the motor-box or by using a second Standa controller.

Software

A LAN cable has to be connected between the dedicated Laptop and the Standa controller. For identifying the IP address for accessing the controller, the *Revealer* program has to be opened. Afterwards the program *XLab* is opened, and the motors can be selected. Important is the correct order when opening in pairs of three (1,2,3; 4,5,6; 7,8,9; 10,11,12) and after each threesome click 'open selected'. Now the selected motors correspond to X-, Y- and Z-axis, respectively. For each of the now open axes, click on 'settings' and 'restore from file'. A window will open, and the file can be selected (von Hamos P(06) is the correct file). If the axes are marked in red, just press the 'STOP' button once in *XLab*.

For flashing the motors to controlling the detector motors, press the red 'Stop' knob on the controller itself first. Change the cables on the patch-box (cf. Fig A.2) and use one cable e.g. from motor 12 and connect it. Afterwards, the axis on the laptop in *XLab*

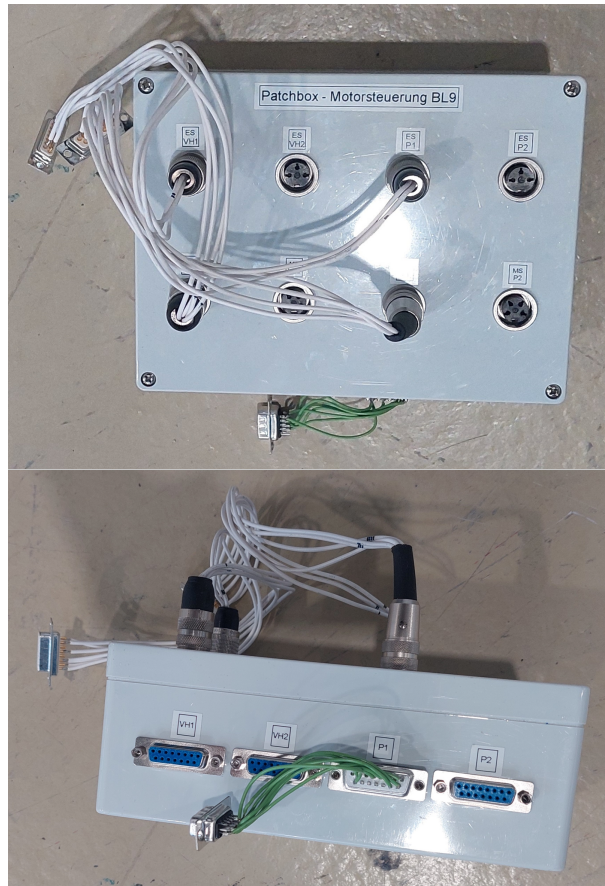


Figure A.2: **top)** top view of the patch-box for connecting the height motors of the spectrometer and detector. **bottom** side view of the patch-box for a connection to a Standa controller used for moving the motors.

needs also new flashing with using the option 'restore from file', select a file with the name 'Nema 17' and 'Nema 23' for Pilatus motors.

A very important note is to never click inside the white box, otherwise the motor moves to arbitrary values and the current position is lost. For securing good motor positions after moving, press 'ZERO', this way the values will be set to zero and the motors can be returned to the zero value after unintentional movement of the motors.

Moving the motors via 'shift' is the best method. This way, values can be entered into the field, a value of 1000 is a big movement, whereas values of 100 to 500 is a smaller movement, when more precision is necessary. For each of the movement, the 'shift' button can be pressed. If the motor limit is reached, the *XLab* window will be red and also the Standa motor lamp lights up red.

Crystal focussing

The first step is a rough first alignment of the crystals on the detector. For this purpose, a small light is placed at the future sample position and a piece of paper in front of the detector window. The experimental hutch has to be dimmed down in order to see the refracted light via the crystals on the paper. The crystals can be moved using the direct control buttons on the Standa controller or via the laptop. The aim is to bring the crystals onto the detector window in the right order.

Subsequently, the fine-tuning is done by using the live detector image outside the experimental hutch with opened shutter. If the crystal signal is cut off, not visible anymore after changing the sample or if the crystals need focussing (thinner, about 2px is good), the Bragg-angle needs to be adjusted. This is done by moving motor 3 or using motor 1 and 2 simultaneously. If the crystal signal should be moved up or down on the detector, motor 2 needs to be moved or motor 1 and 3 simultaneously. Sometimes, the simultaneous movement of the crystals needs to be used, if one of the motors hit a hard limit in their movement.

Further information can be found in the doctoral thesis of Dr. Christian Thiering [115].

A.5 Diamond damages – why diamonds are consumables for us

Here is a small picture archive of damaged diamonds. It portrays the variety in which the diamonds can crack, break or crumble. The types of damages are roughly categorized.

A.5.1 Culet cracks

Starting with a small crack on the culet, these diamonds can still be used for low pressures. It depends on the extent of crack, but roughly 20 GPa could be achievable. This kind of damage is visible in figure A.3, A.4 and A.5.

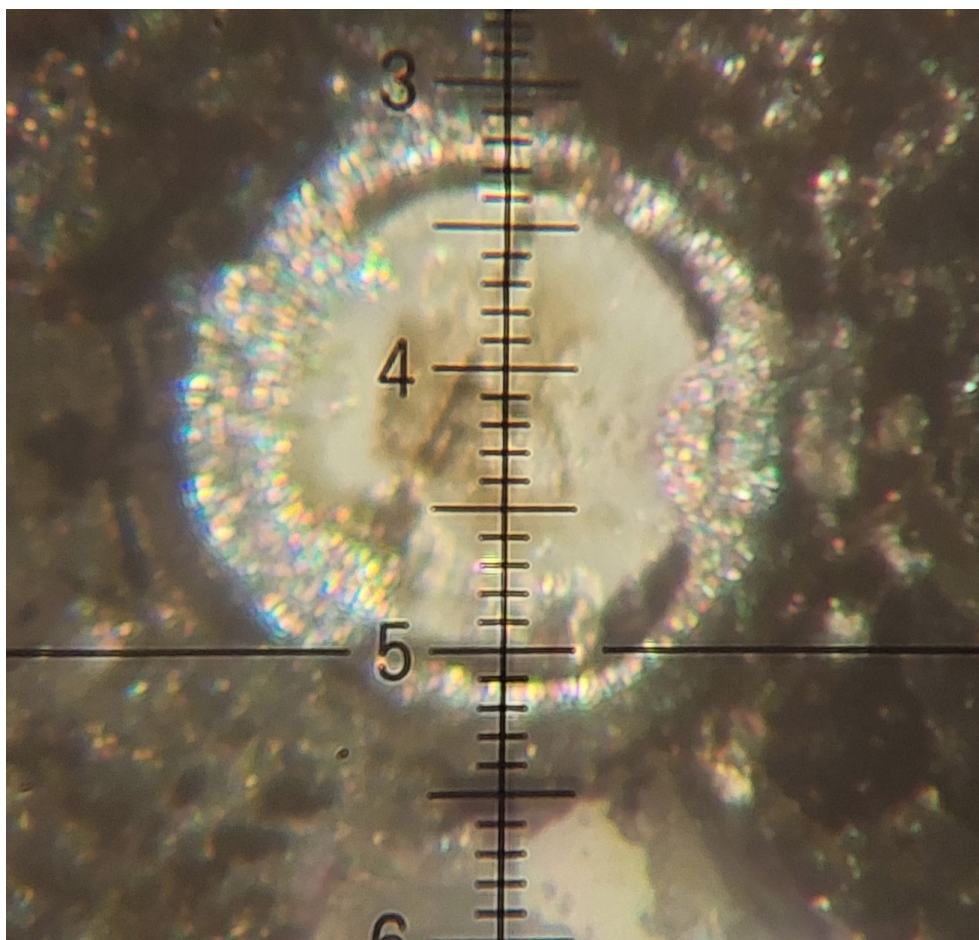


Figure A.3: Photo of a culet crack diagonally across the whole culet. Around the culet the rhenium gasket is still in place.

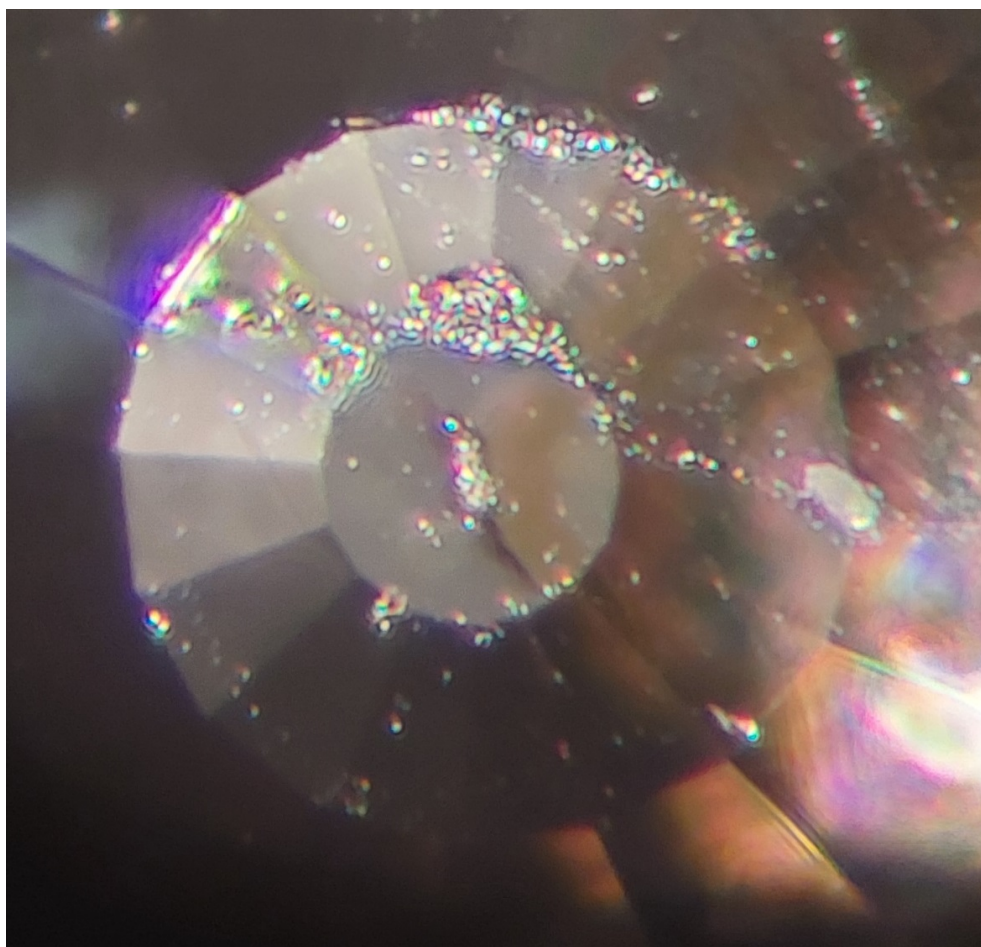


Figure A.4: Photo of culet crack, which does not cover the whole culet. The white speckles are dirt. Side note: this is a dirty diamond and this kind of mucky diamond could not be used while preparing a diamond anvil cell.

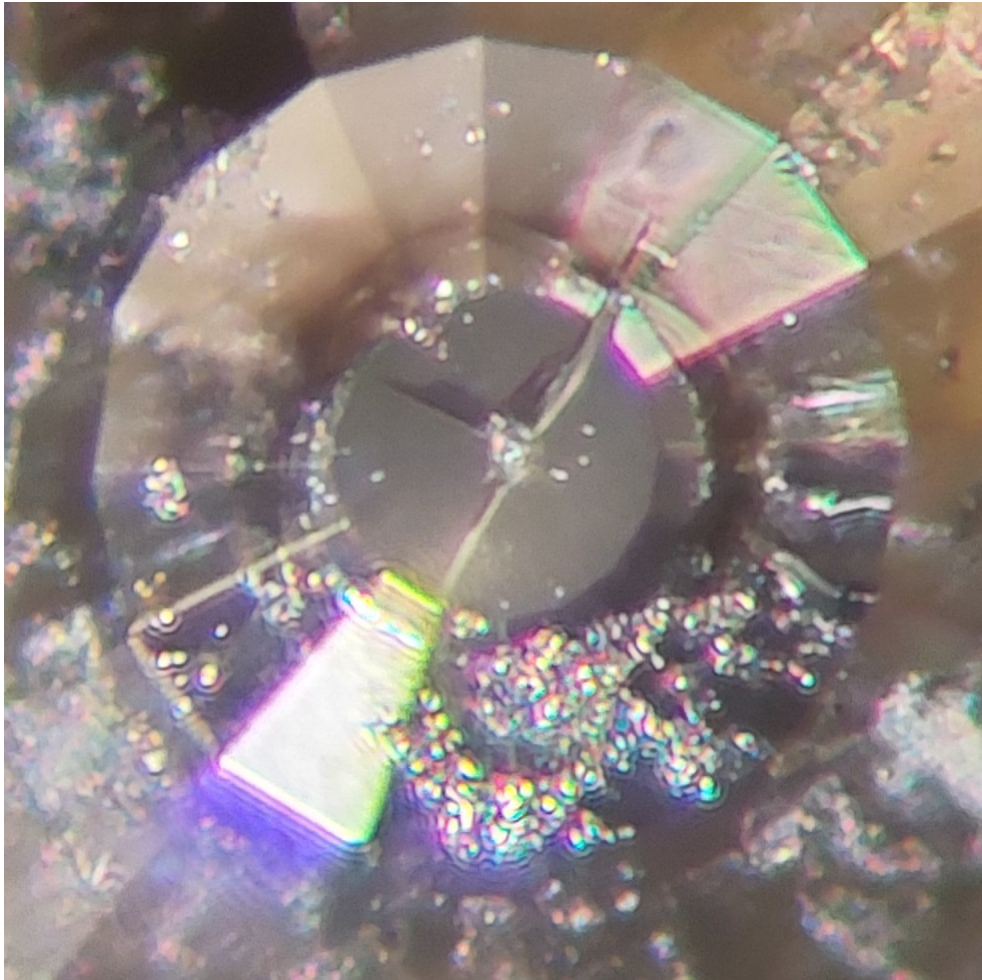


Figure A.5: Photo of another culet crack, this is more of a cross crack and it also shows a bit of a ring crack around the culet.

A.5.2 Ring cracks

A different form of crack is the ring crack around the culet of the diamond as seen in figure A.6, figure A.7 and a more severe form in figure A.8, which is considered broken.

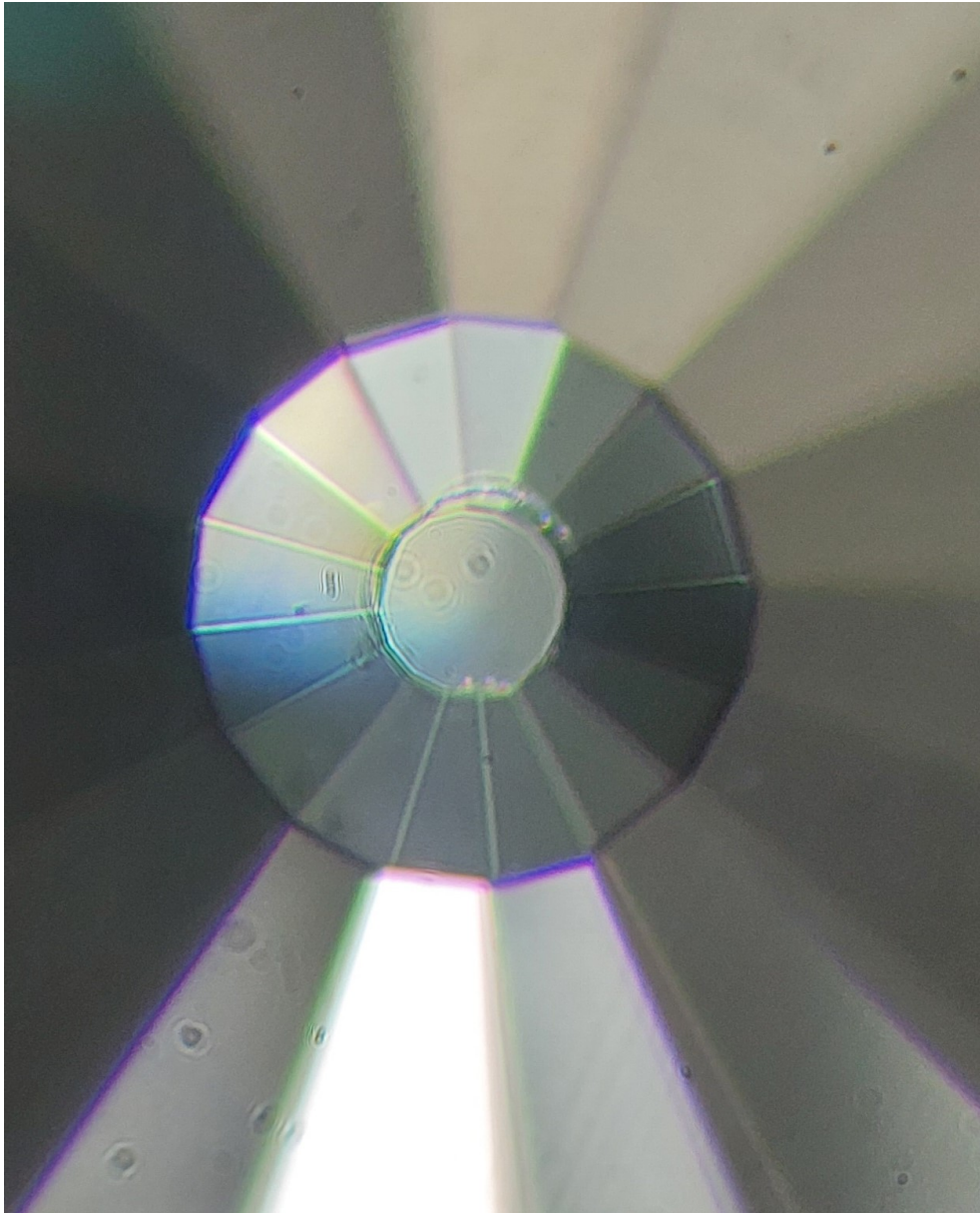


Figure A.6: Photo of ring crack around the culet. Side note: this is considered a properly cleaned diamond.

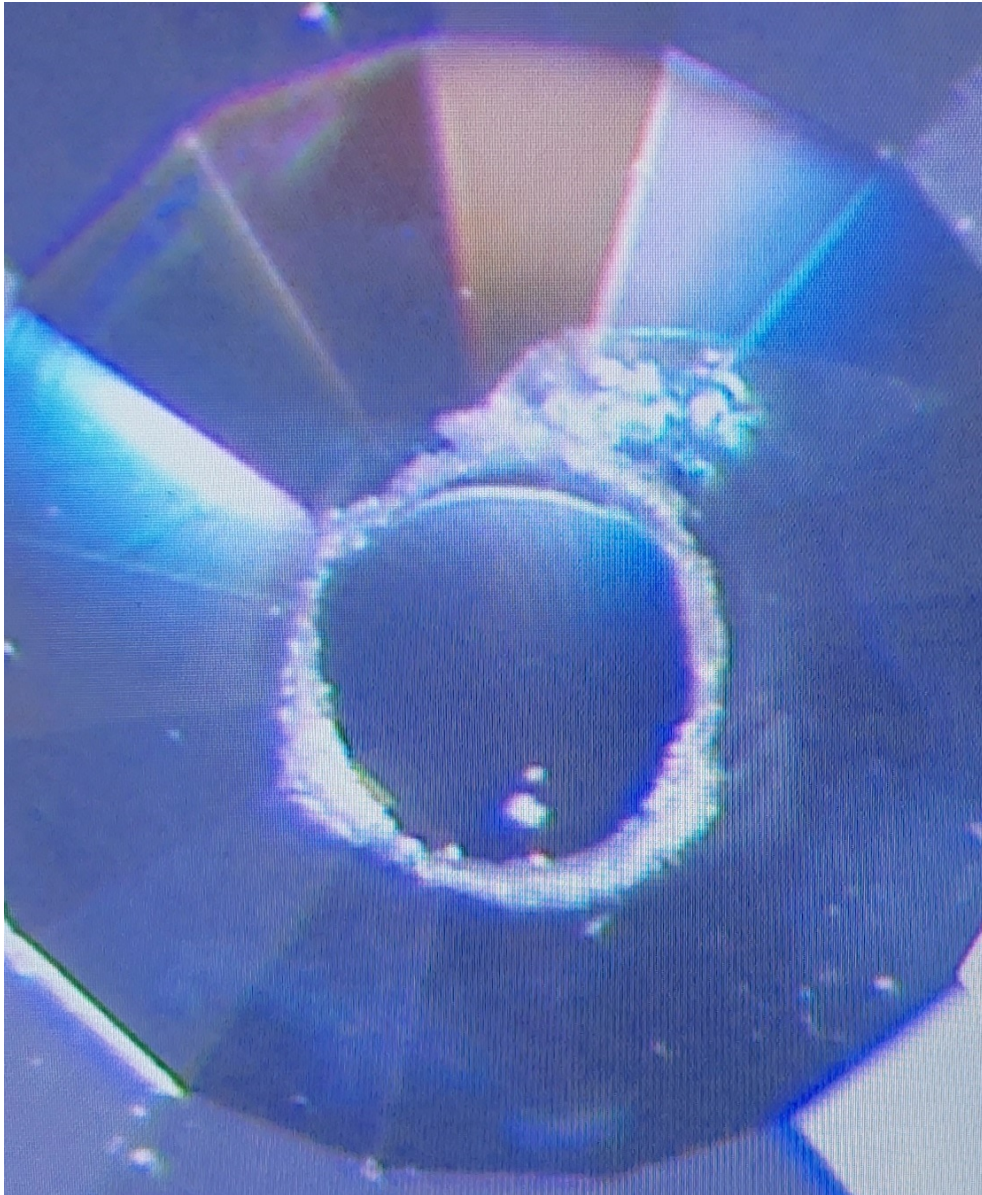


Figure A.7: Photo of a slightly more severe ring crack around the culet with the damage protruding into the pavilion area.

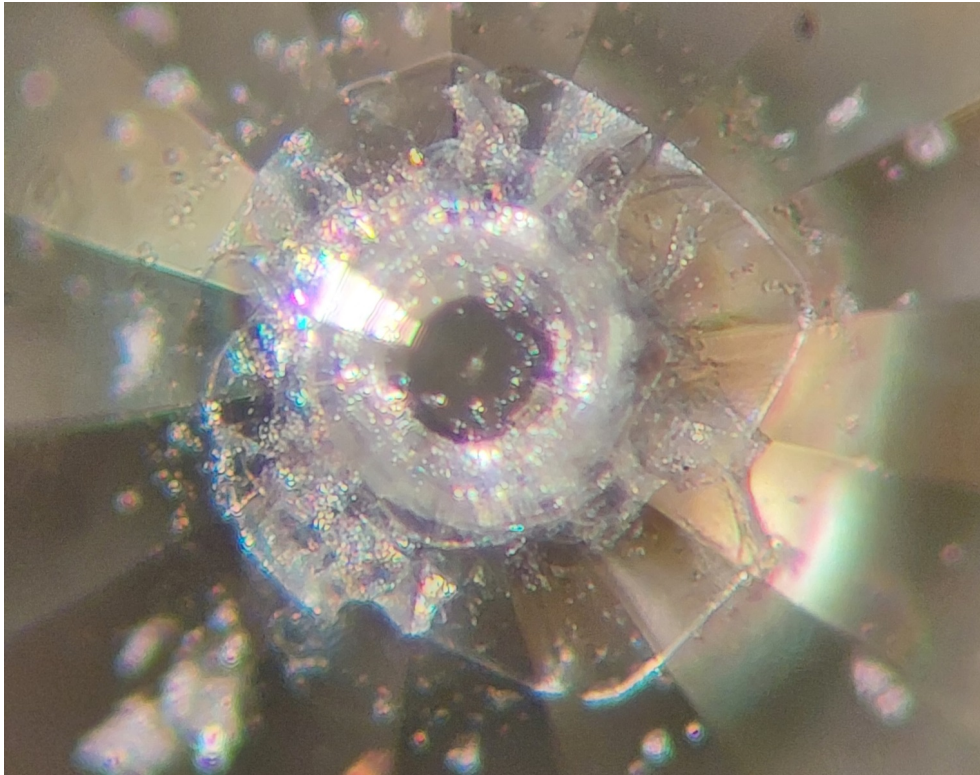


Figure A.8: Photo of a severe ring crack around the culet, this is also known as broken.

A.5.3 Backside cracks

Not only the front side, i.e. the culet, can break, but also the back of the diamond. Two photos of backside cracks are presented in figure A.9 and a backside crack still visible in a broken diamond in figure A.9.

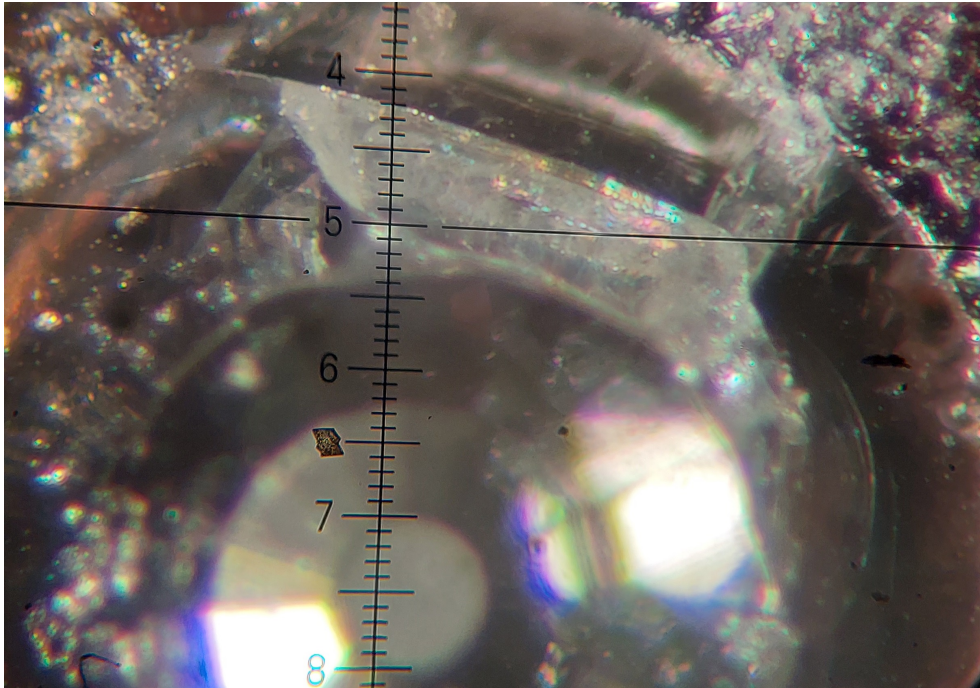


Figure A.9: Photo of the back of a diamond with a crack. In the background the culet is visible.

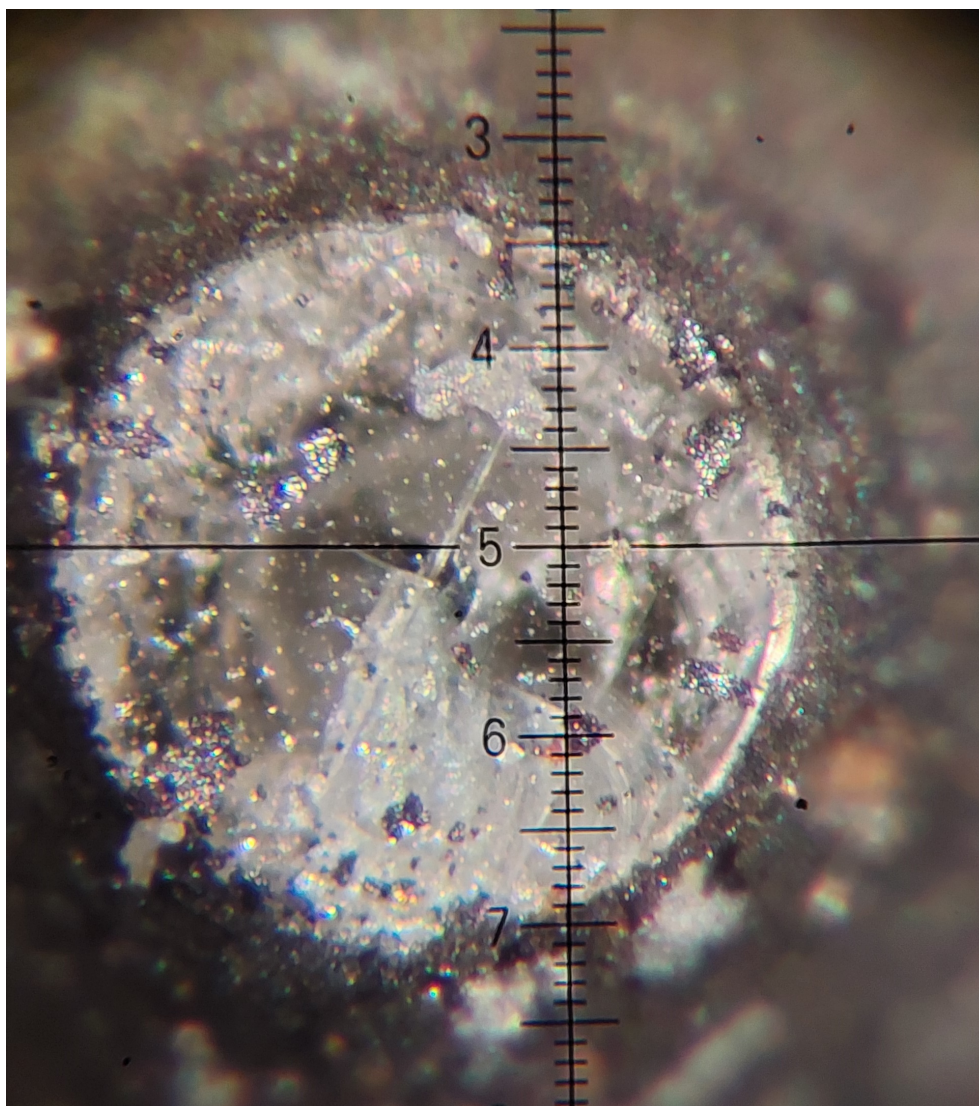


Figure A.10: Photo of the back of a diamond with a severe crack, which is more considered broken already. The view is through the diamond seat from outside the cell.

A.5.4 Severely broken

The last category is severely broken (Fig. A.11) and exploded diamonds in figure A.12 and figure A.13 with the gasket of the latter figure, where the diamond once was in figure A.14.

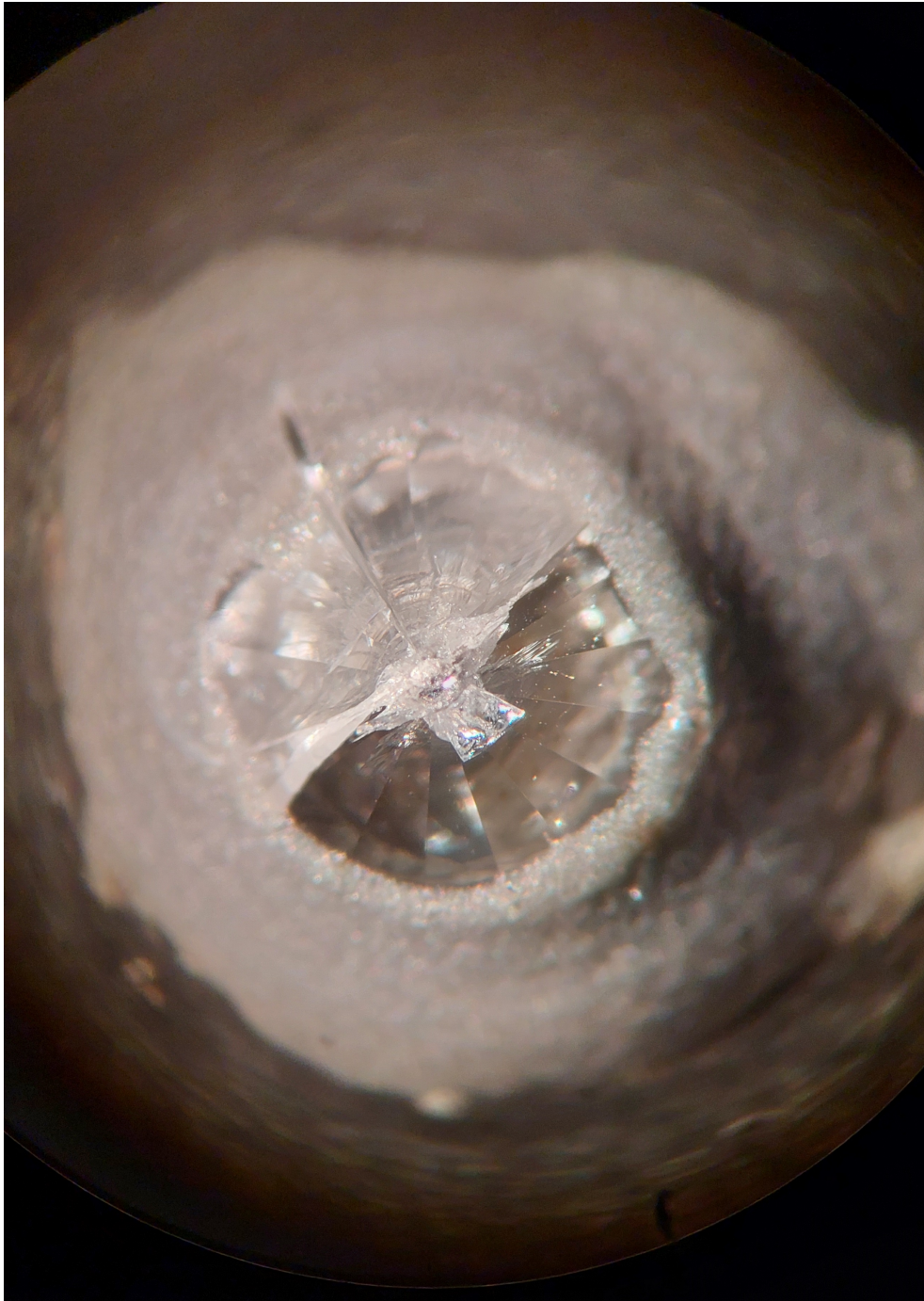


Figure A.11: Photo of an ST with one half completely shattered still glued onto the seat.



Figure A.12: Photo of nearly only diamond dust. The pavilion planes and culet are still recognizable, but the outer parts are scattered across the seat.

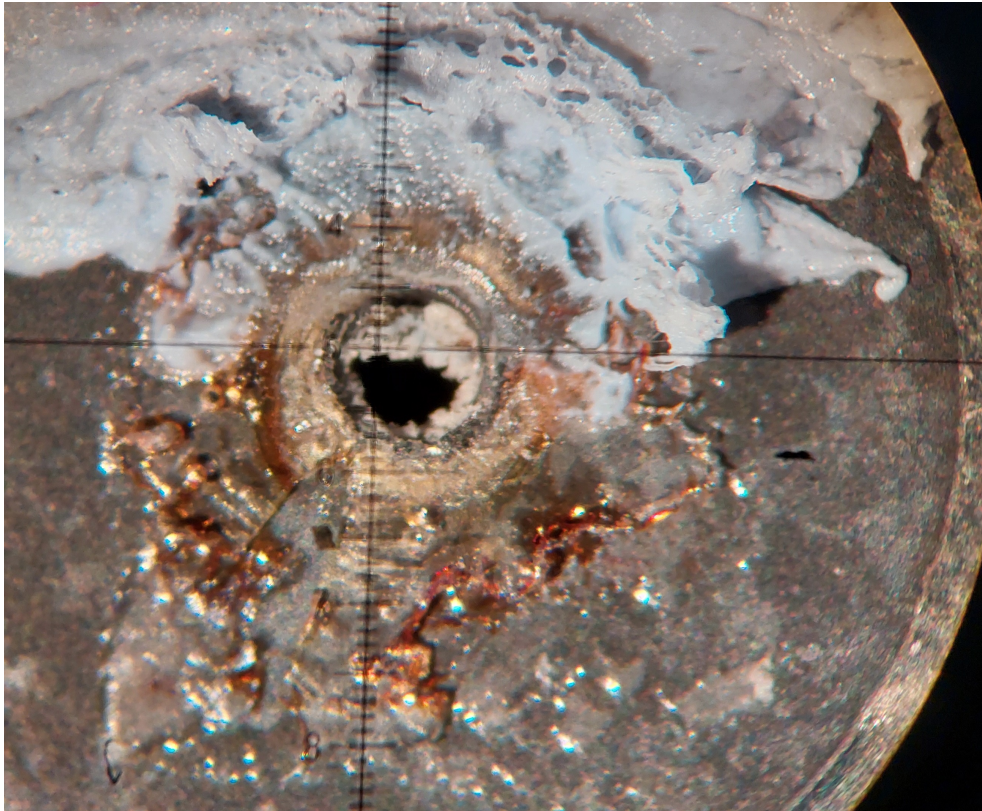


Figure A.13: Photo a MD seat, where some small parts are scattered across, and the diamond dust is in the hole of the seat at the edges. The Blu Tack is visible on top, which held the gasket.

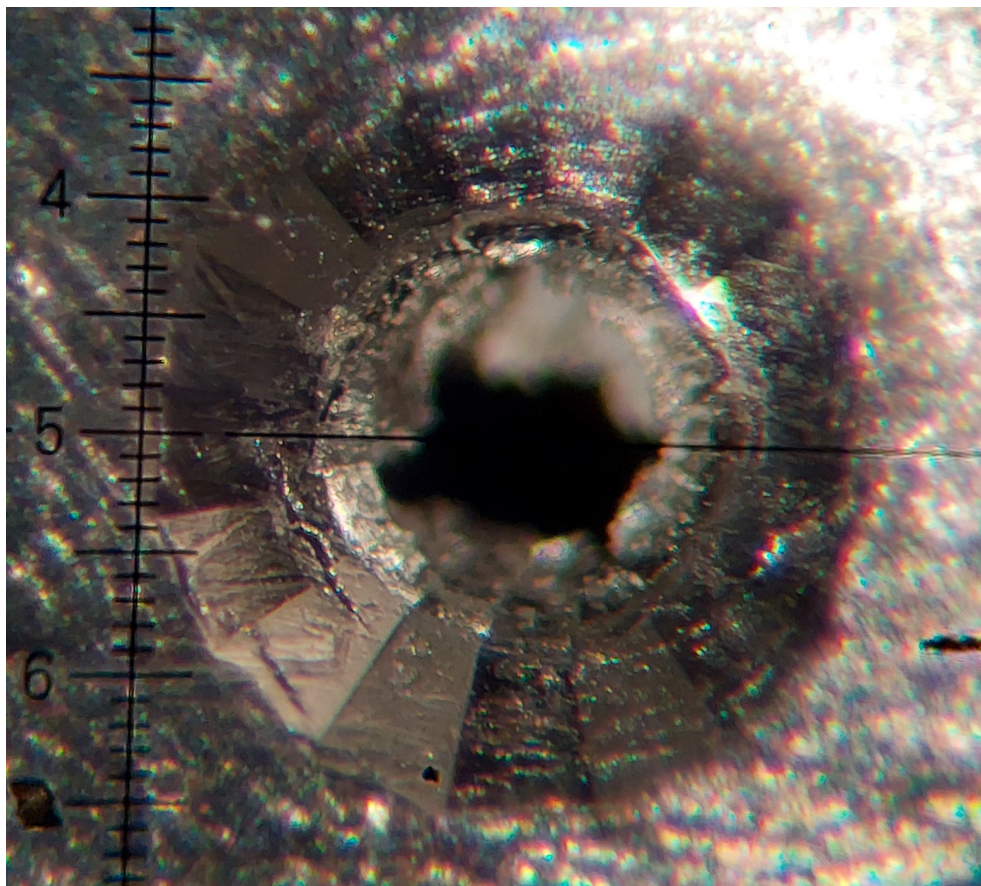


Figure A.14: Photo the gasket and due to the impact of the diamond's breakage, the whole culet area of the gasket is gone. Bits of diamond dust are still visible in white.

A.6 Pictures from beamline setup

A.6.1 P01

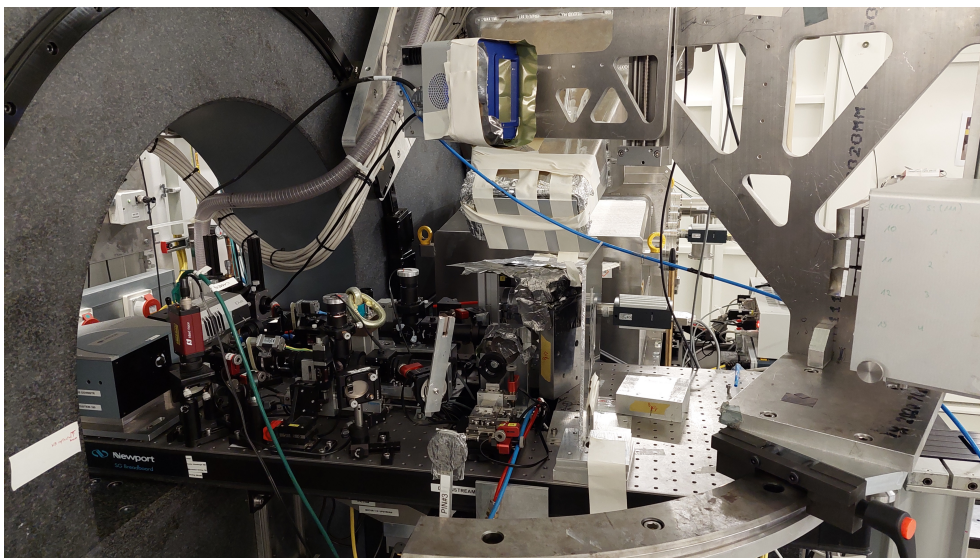


Figure A.15: Photo the experimental setup at P01 including the laser-heating system on a pegboard and the von Hámós spectrometer.

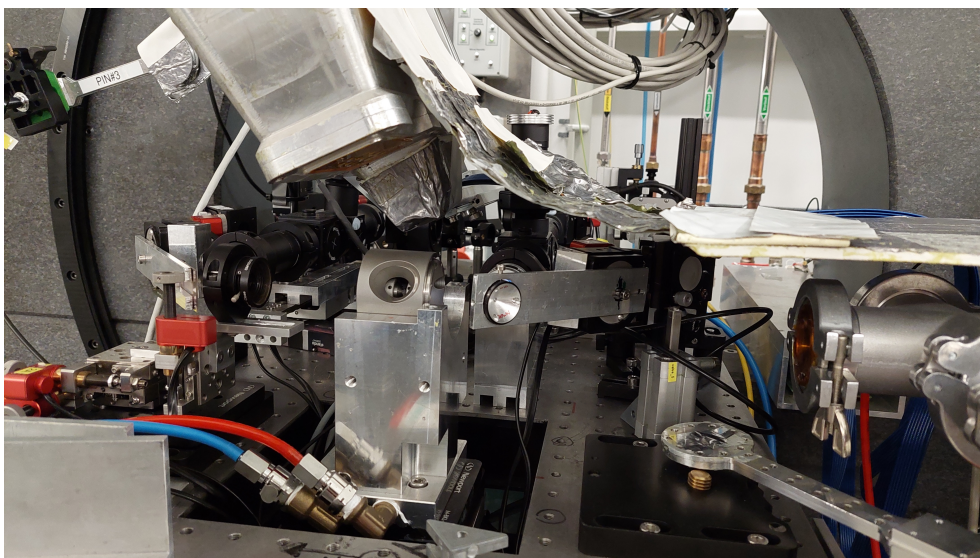


Figure A.16: Side-view photo the experimental setup at P01 with a view of the DAC in its holder integrated into the laser-heating system.

A.6.2 ID20

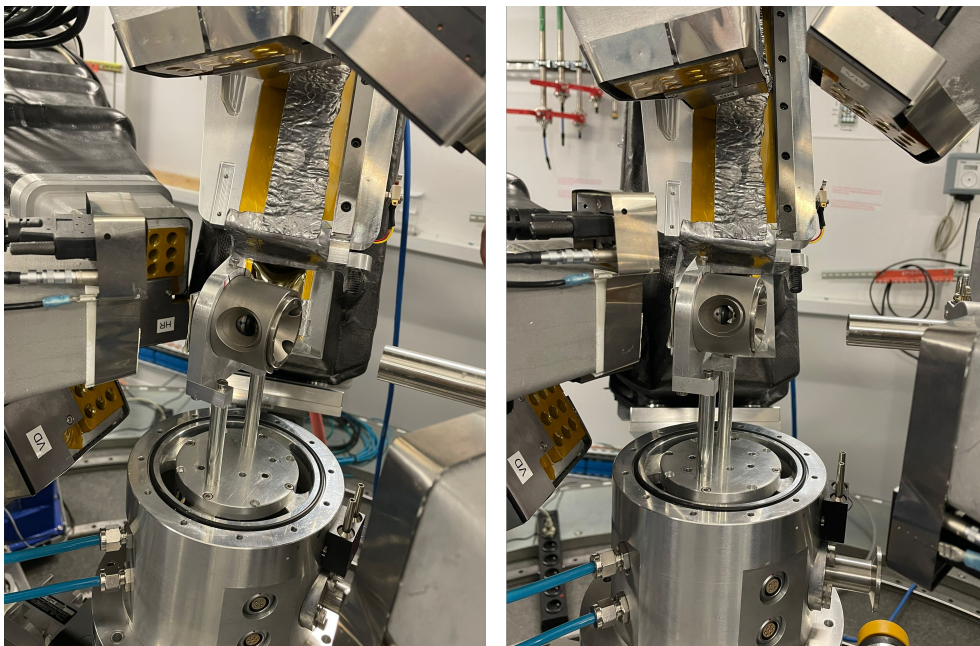


Figure A.17: Photos the experimental setup at ID20 including the DAC in its holder, behind the von Hámos spectrometer inside a vacuum chamber.

A.7 Fe_2O_3

A.7.1 XES

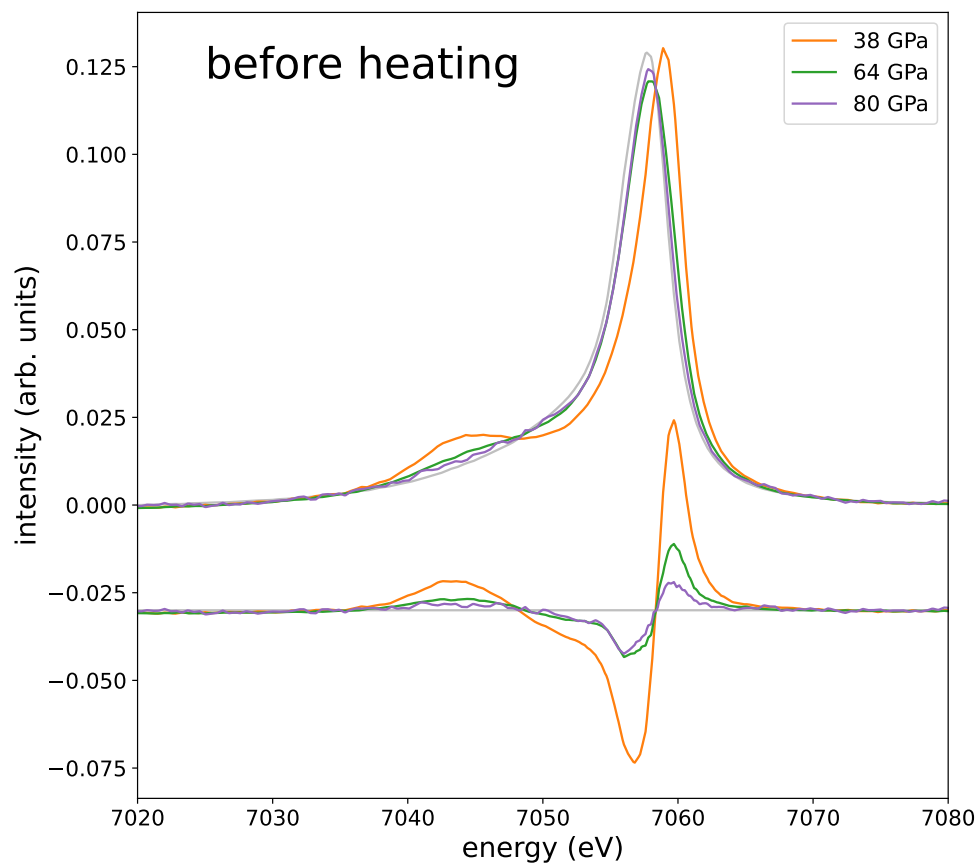


Figure A.18: XES spectra at room temperature, i.e. before heating, at 38, 64 and 80 GPa.

A.7.2 XRD

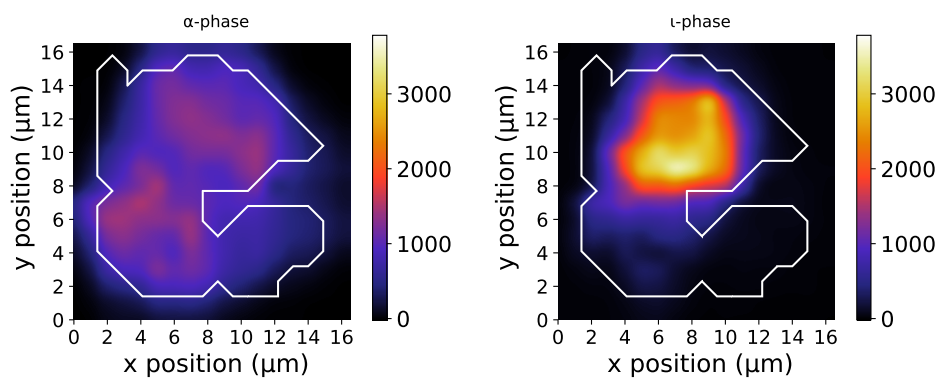


Figure A.19: XRD 2D-map at 38 GPa with the sample outline without normalization.

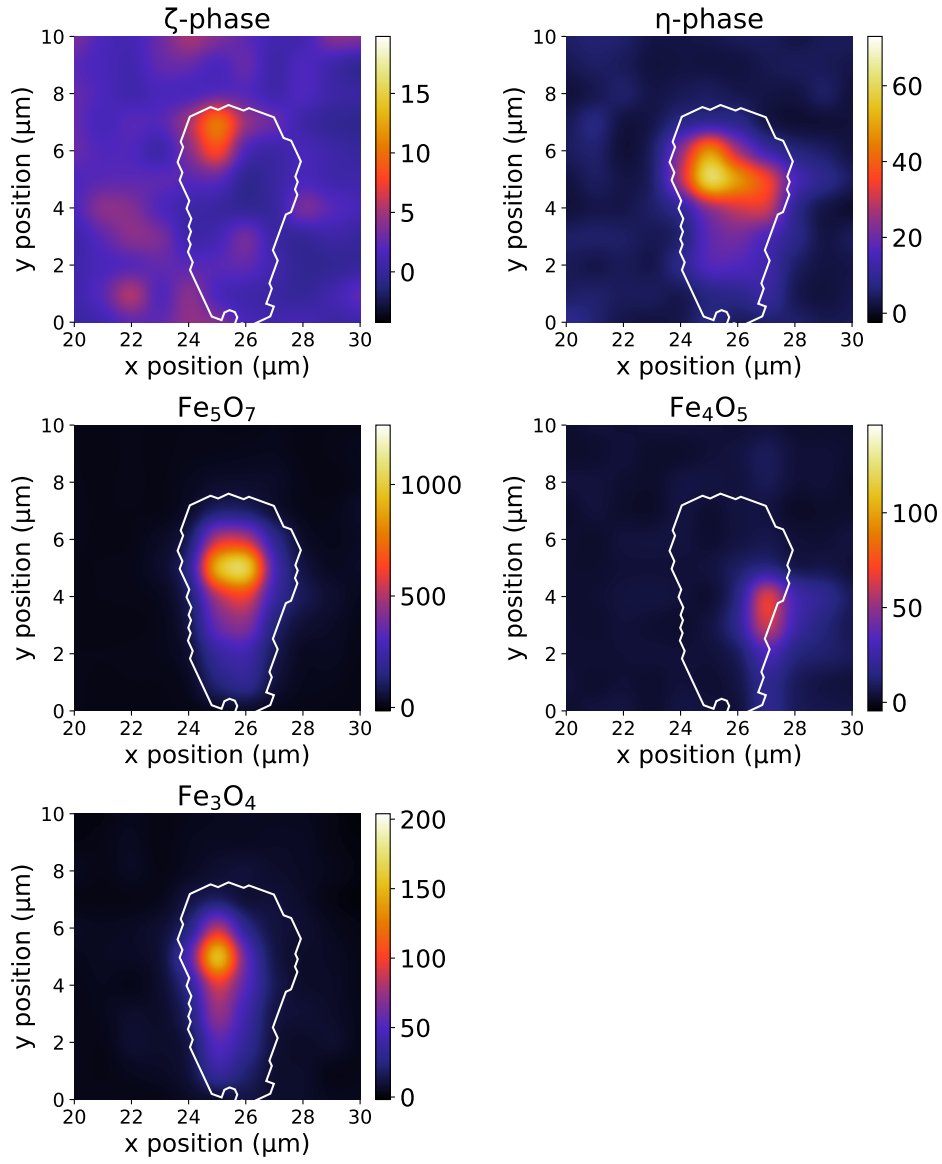


Figure A.20: XRD 2D-map at 64 GPa with the sample outline without normalization.

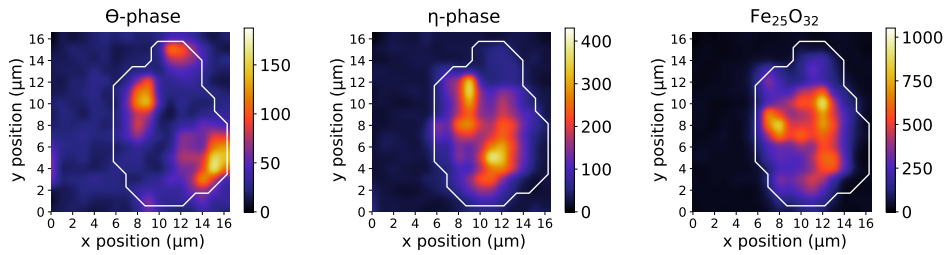


Figure A.21: XRD 2D-map at 80 GPa with the sample outline without normalization.

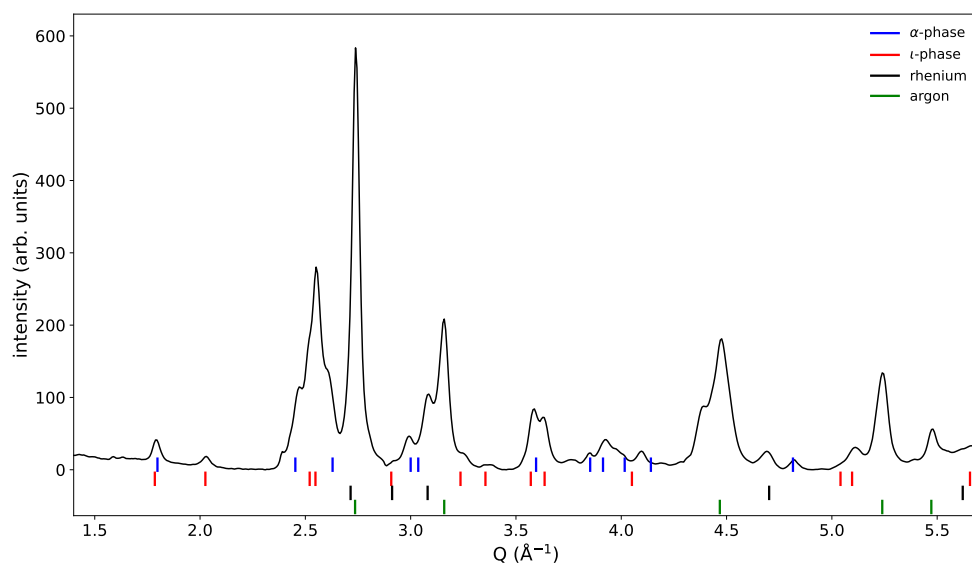


Figure A.22: Integrated diffraction pattern at 38 image 162 with used reflexes underneath of each.

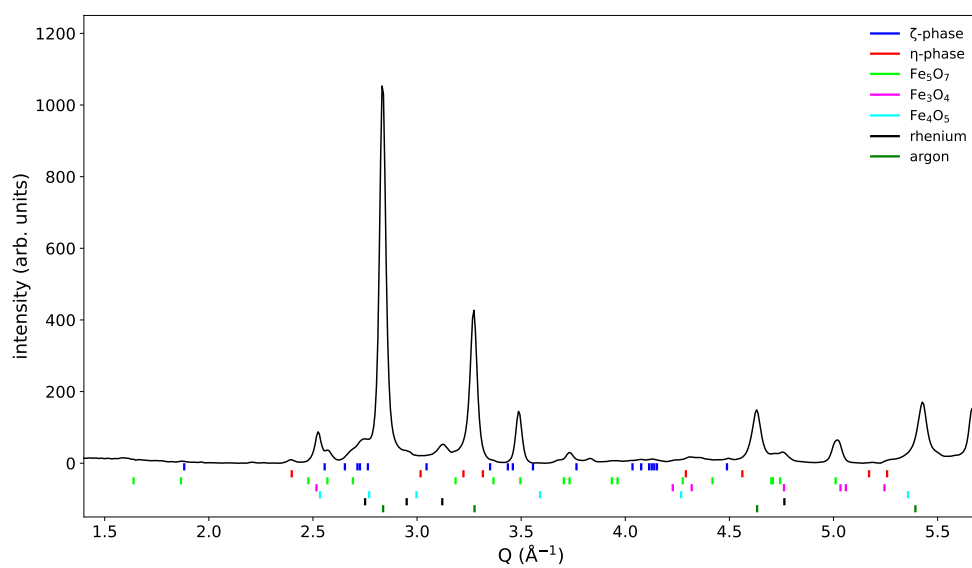


Figure A.23: Integrated diffraction pattern at 64 image 160 with used reflexes underneath of each.

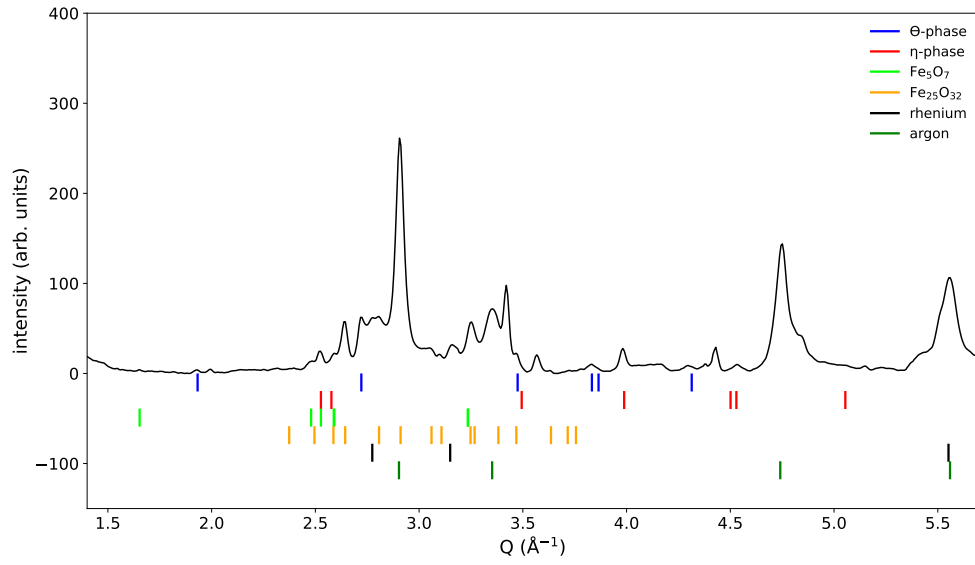


Figure A.24: Integrated diffraction pattern at 80 GPa image 179 with used reflexes underneath of each.

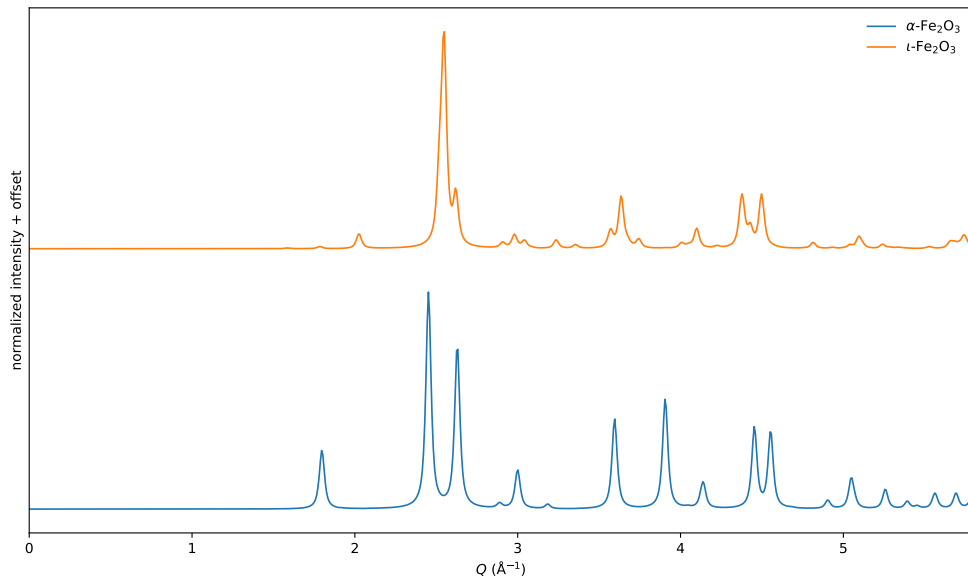


Figure A.25: Powder patter at 38 of α- and ι-Fe₂O₃ phases.

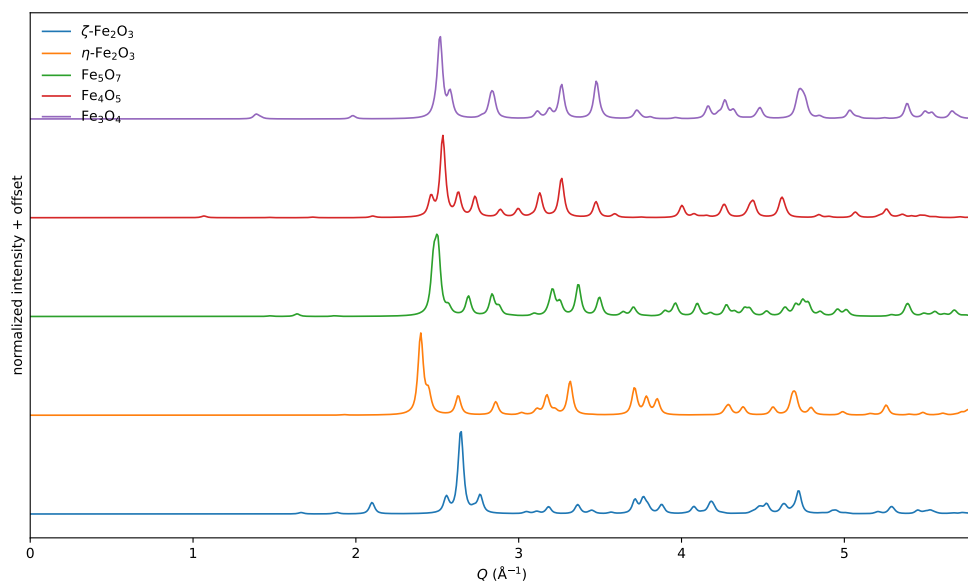


Figure A.26: Powder pattern at 64 K of ζ - and η - Fe_2O_3 phases, Fe_3O_4 , Fe_4O_5 and Fe_5O_7 .

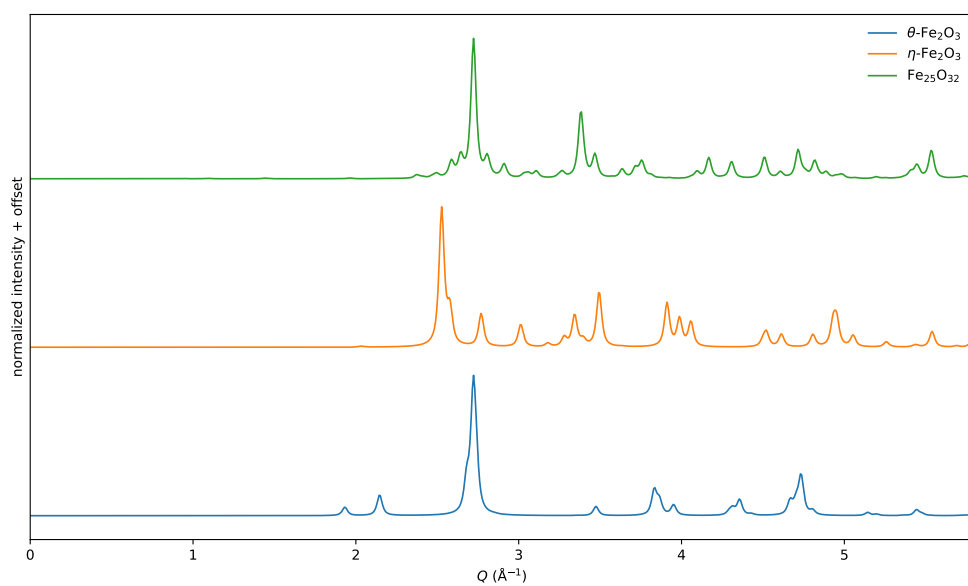


Figure A.27: Powder pattern at 80 K of θ - and η - Fe_2O_3 phases and $\text{Fe}_{25}\text{O}_{32}$.

A.7.3 Tables

Table A.7: Gaussian fit results for the $K\beta_{2,5}$ peak in the vtc spectra of Fe_2O_3 . The peak center μ and full width at half maximum (FWHM) were obtained from Gaussian fits. Energy shifts ΔE are given relative to the room-temperature spectrum (b heat) at the respective pressure.

Pressure	Condition	μ (eV)	FWHM (eV)	ΔE (eV)
38 GPa	300 K	7105.717 ± 0.065	4.100 ± 0.385	$+0.000 \pm 0.092$
	2026 K	7106.452 ± 0.054	5.652 ± 0.622	$+0.735 \pm 0.085$
	1975 K	7106.727 ± 0.069	7.064 ± 1.102	$+1.010 \pm 0.095$
	2000 K	7106.578 ± 0.081	5.721 ± 0.868	$+0.861 \pm 0.104$
	quenched	7105.341 ± 0.051	7.064 ± 0.872	-0.376 ± 0.083
64 GPa	300 K	7103.578 ± 0.019	7.064 ± 0.212	$+0.000 \pm 0.027$
	2190 K	7103.446 ± 0.045	7.064 ± 0.459	-0.132 ± 0.049
	2065 K	7103.443 ± 0.070	7.064 ± 0.715	-0.135 ± 0.073
	2067 K	7103.052 ± 0.032	7.064 ± 0.256	-0.526 ± 0.037
	quenched	7103.535 ± 0.022	7.064 ± 0.242	-0.043 ± 0.029
80 GPa	300 K	7103.785 ± 0.067	7.064 ± 0.728	$+0.000 \pm 0.095$
	1870 K	7104.123 ± 0.048	7.064 ± 0.677	$+0.338 \pm 0.082$
	1940 K	7103.238 ± 0.118	2.022 ± 0.325	-0.546 ± 0.135
	2470 K	7103.420 ± 0.052	4.377 ± 0.215	-0.365 ± 0.085
	quenched	7104.601 ± 0.076	7.064 ± 1.644	$+0.816 \pm 0.101$

Table A.8: Interatomic distances ($\text{\AA}$) for different iron oxide phases at 38, 64, and 80 GPa. Extracted from CIF file at the given pressures.

ressure (GPa)	38		64		80		
Phase	α	ι	ζ	η	Fe_5O_7	θ	$\text{Fe}_{25}\text{O}_{32}$
CIF pressure (GPa)	45	43	55	56	56	76	85
distances ($\text{\AA}$)							1.92314
							1.92314
							1.92314
							1.92314
							1.92314
							1.92314
							1.80416
							1.79614
							1.79614
							1.80416
							1.85814
							1.85814
							1.77413
			1.82508		1.853		1.84016
			1.82508		1.87819		1.84016
			1.85037		1.87819		1.77413
			1.85037	1.87811	1.853		1.81514
			1.91725	1.8177	1.87819	1.7821	1.81514
			1.91725	1.87811	1.87819	1.7247	1.74118
			1.87295	1.87811	2.082	1.7821	1.76114
	2.0056	1.88916	1.89032	1.8177	1.96615	1.824	1.7247
	1.84583	1.98013	1.89544	1.87811	1.96615	1.855	1.7821
	2.0056	2.144	1.91812	1.96812	2.043	1.845	1.95013
	1.84583	1.976	2.15293	1.96812	2.043	1.785	1.95013
	2.0056	1.8819	2.17969	2.21719	1.912	1.805	2.10418
	1.84583	1.804	2.3885	2.05514	1.912	1.766	1.86812
			2.41208	2.05514	1.753		1.86812
			1.77274	2.05514	1.8664		2.10418
			1.77274	2.05514	1.8664		1.95013
			1.78454	2.21719	1.863		1.96015
			1.78454		1.923		2.0705
			1.78615		1.923		1.96714
			1.78615				1.96714
							1.9529
							1.9529
							2.1806
							1.95311
							1.95311
							1.9401
							1.9401
							1.9833
							1.9833
							1.9421
							1.9421
							2.3574

Table A.9: Average Fe-O bond lengths, polyhedral distributions, and calculated spin states for the investigated phases.

Phase	α	ι	ζ	η	Fe_3O_7	θ	η	$\text{Fe}_{25}\text{O}_{32}$	$\beta\text{-Fe}_3\text{O}_4$	$\delta\text{-Fe}_3\text{O}_4$
avg. bond length										
per polyhedra (Å)	1.9257	1.9432	1.8642 2.0888 1.7811	1.8575 2.0738	1.8672 1.985 1.8657	1.8094	1.7627 1.968	1.9231 1.8192 1.8098 1.7795 1.9884 1.989 2.0122	1.8733 1.9414	1.869 2.158
number ppuc	24	8	21	21	22	8	21	55	18	18
polyhedral V (Å ³)			6×15.4004 9×8.6193 6×7.5206	6×15.2359 15×8.4038	6×10.8727 10×8.5855 6×8.5379	6×13.0209 15×7.1821	6×11.1131 5×10.9378 6×10.6641 10×8.0089 10×7.8991 10×7.4962 8×6.7684	12×8.6779 6×6.8973	18×14.3054	
calculated spin	2.5	2.5	1.0714	1.0714	1.0455	0.5	1.0714	1.1182	1.8333	2.5

A.7.4 RXES maps

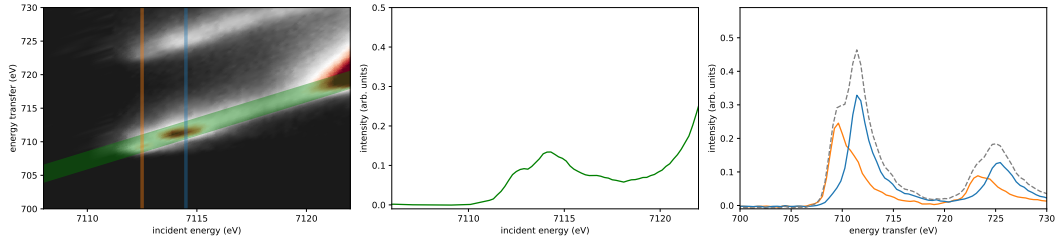


Figure A.28: Exemplary RXES map at 38 GPa before heating (**left**) with CEE cut (green) and CIE cut (red) and its spectra (**right**). **Right top** spectra from the CEE cut, namely the HERFD-XANES spectra and **right bottom** spectra from CIE cut, with L-edge like information.

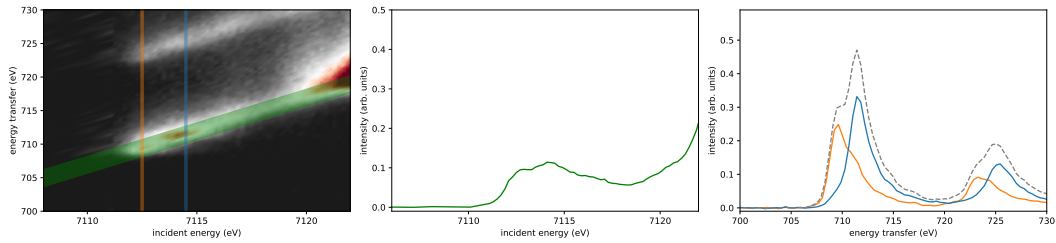


Figure A.29: Exemplary RXES map at 38 GPa after heating (**left**) with CEE cut (green) and CIE cut (red) and its spectra (**right**). **Right top** spectra from the CEE cut, namely the HERFD-XANES spectra and **right bottom** spectra from CIE cut, with L-edge like information.

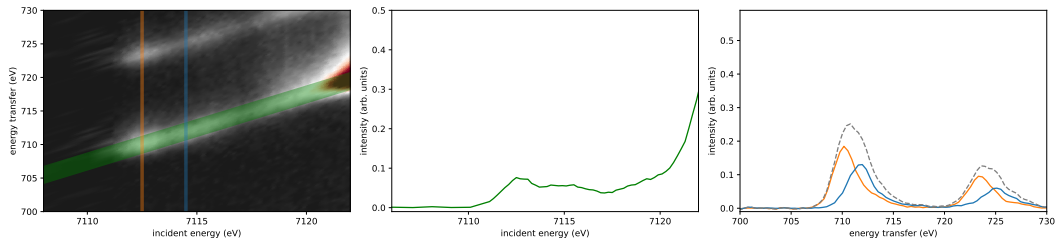


Figure A.30: Exemplary RXES map at 64 GPa before heating (**left**) with CEE cut (green) and CIE cut (red) and its spectra (**right**). **Right top** spectra from the CEE cut, namely the HERFD-XANES spectra and **right bottom** spectra from CIE cut, with L-edge like information.

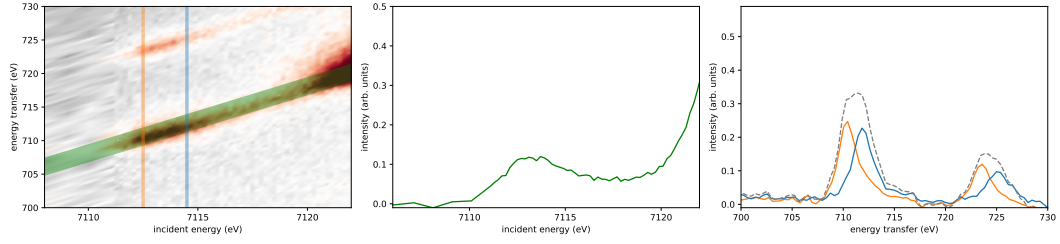


Figure A.31: Exemplary RXES map at 80 GPa before heating (**left**) with CEE cut (green) and CIE cut (red) and its spectra (**right**). **Right top** spectra from the CEE cut, namely the HERFD-XANES spectra and **right bottom** spectra from CIE cut, with L-edge like information.

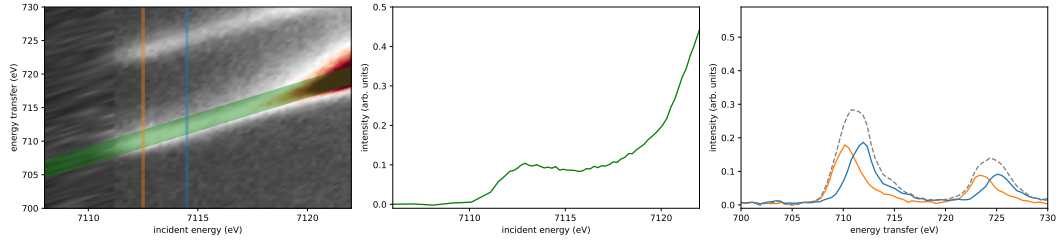


Figure A.32: Exemplary RXES map at 80 GPa after heating (**left**) with CEE cut (green) and CIE cut (red) and its spectra (**right**). **Right top** spectra from the CEE cut, namely the HERFD-XANES spectra and **right bottom** spectra from CIE cut, with L-edge like information.

A.8 Haplobasaltic glasses



(a) ID20 (XES)



(b) ID18 (SMS)

Figure A.33: Ambient HBG samples on sample holders before measurements. (a) ID20 setup (XES) using scotch tape, showing samples before (top) and after (bottom) measurement. (b) ID18 setup (SMS) using Kapton tape. Sample compositions: HBG 1 (61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$), HBG 2 (47%), HBG 3 (13%).

A.8.1 SMS spectra with fit at pressure

All the subsequent plot include data represented by black crosses, the fit as a black line and Fe^{2+} (doublet 1), Fe^{3+} (doublet 2), and the Be-lens contribution (doublet 3) as colored areas. Underneath the plot, the residuals of the fit are shown.

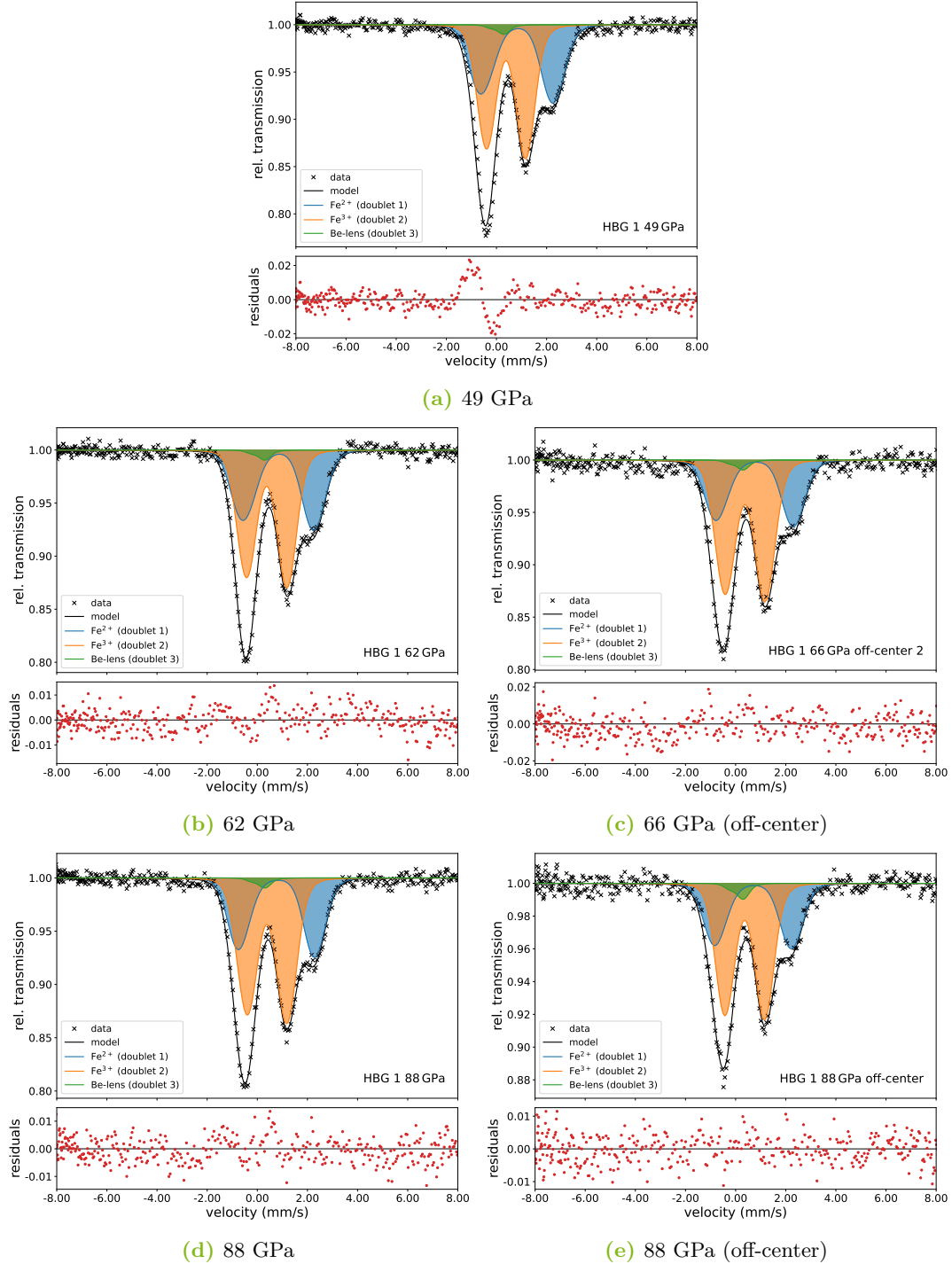


Figure A.34: SMS spectra of HBG 1 (61% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) at different pressures and positions.

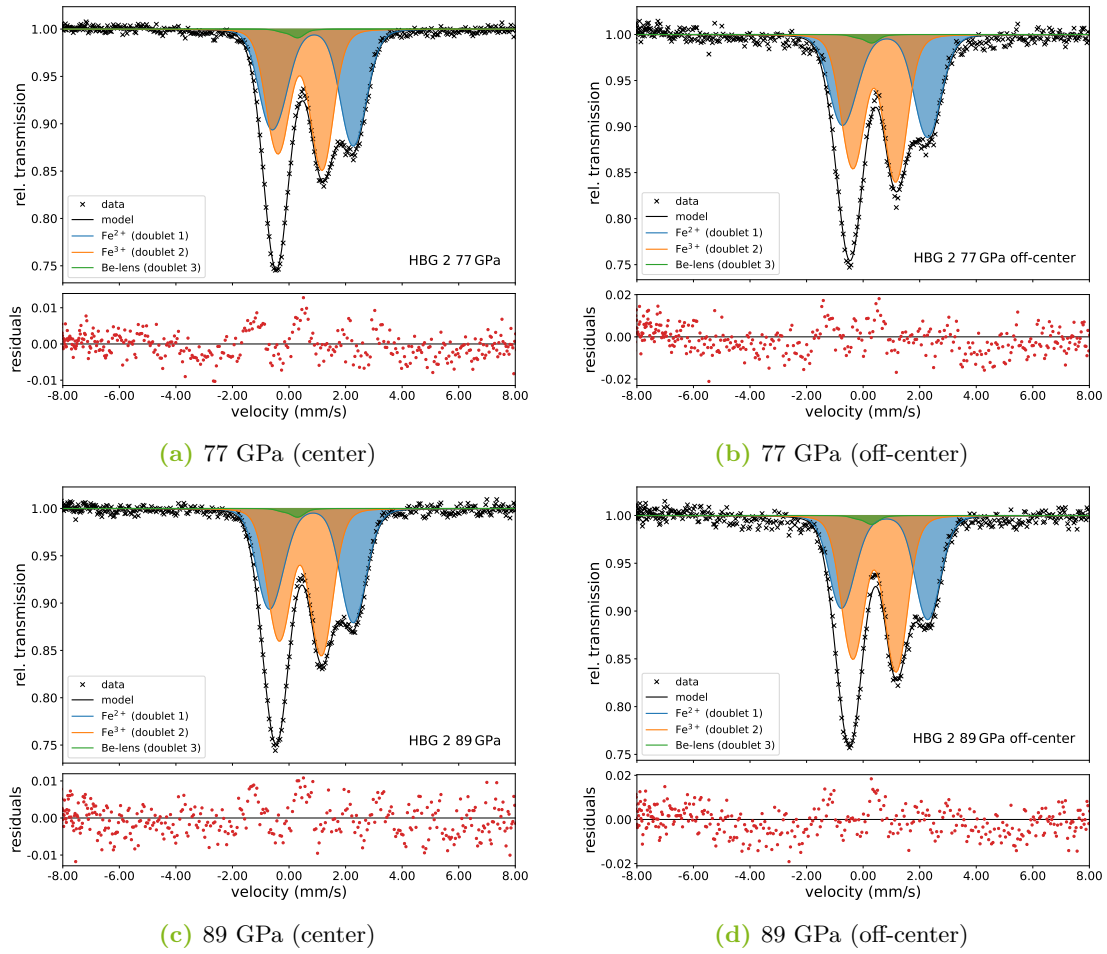


Figure A.35: SMS spectra of HBG 2 (47% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) at 77 and 89 GPa, measured at center and off-center positions.

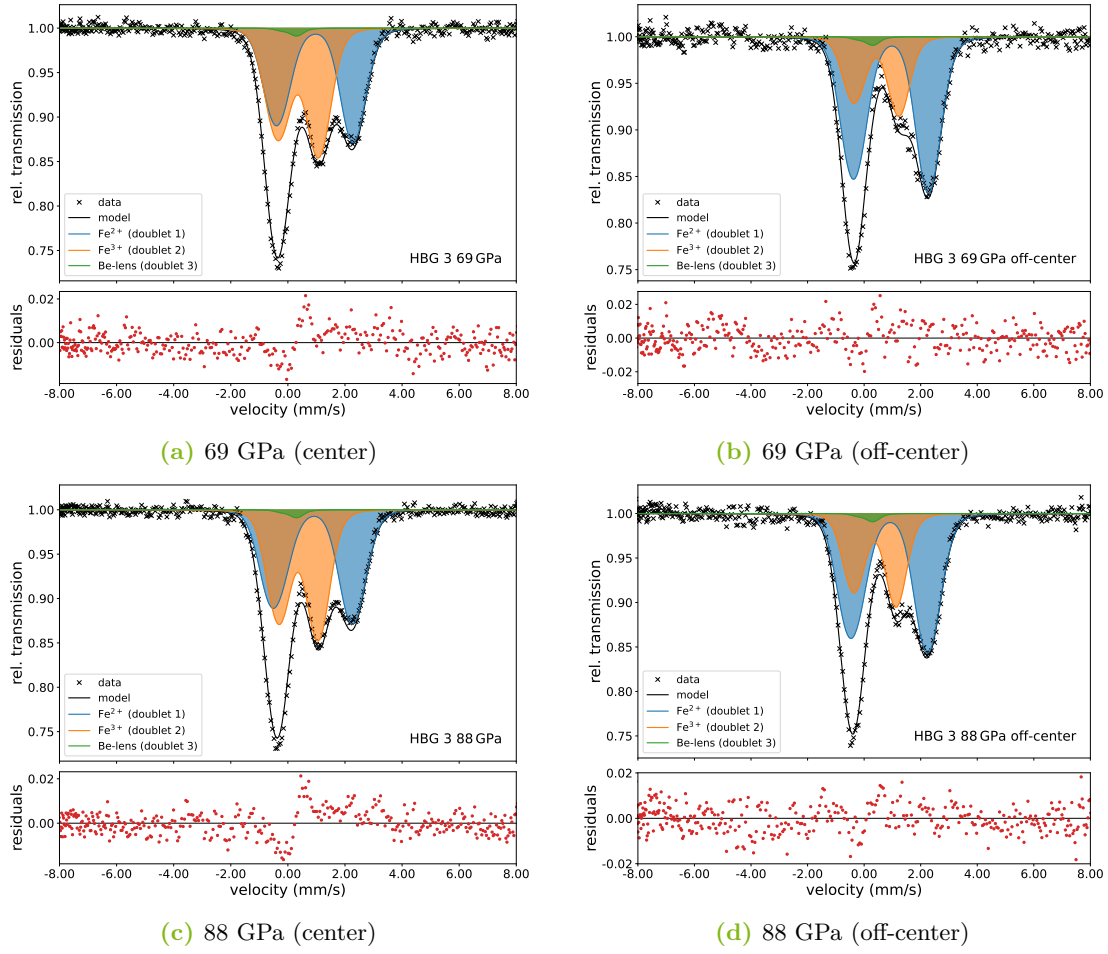


Figure A.36: SMS spectra of HBG 3 (13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) at 69 and 88 GPa, measured at center and off-center positions.

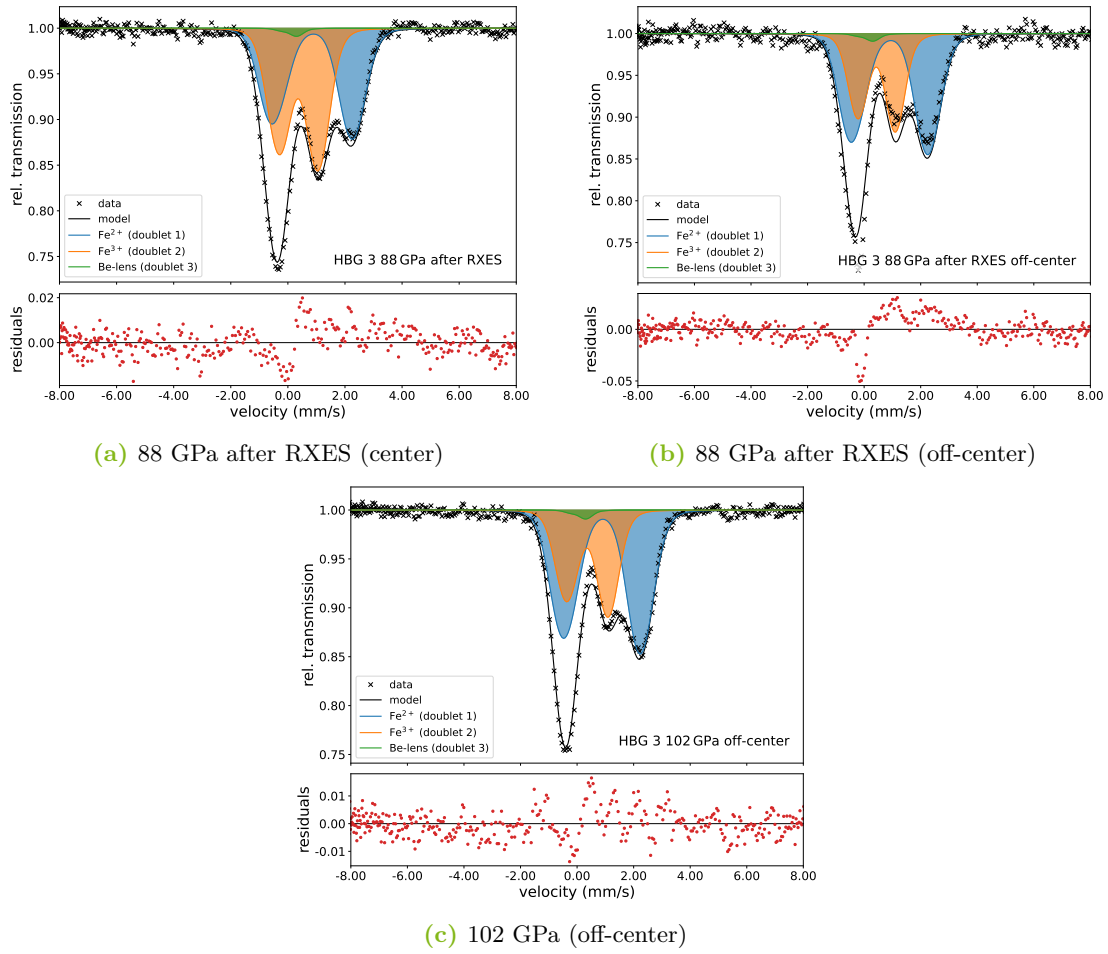


Figure A.37: SMS spectra of HBG 3 (13% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$) at 88 GPa after RXES center and off-center and at 102 GPa off-center.

A.8.2 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio calculation tables

Table A.10: $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios derived from SMS measurements for HBG 1 (61%) as a function of pressure. Off-center measurements correspond to spectra recorded at slightly displaced positions within the sample chamber.

pressure (GPa)	$\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (%)	comment
0	64.51	
38	53.60	
49	58.70	
62	59.54	
66	59.94	
66	64.51	off-center 1
66	65.89	off-center 2
88	63.55	
88	64.00	off-center
100	65.59	

Table A.11: $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios derived from SMS measurements for HBG 2 (47%) as a function of pressure. Off-center measurements correspond to spectra recorded at slightly displaced positions within the sample chamber.

pressure (GPa)	$\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (%)	comment
0	51.03	
18	40.11	
62	46.45	
62	50.97	
77	51.64	
77	55.79	off-center
89	54.01	
89	58.04	off-center
118	58.79	

Table A.12: $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios derived from SMS measurements for HBG 3 (13%) as a function of pressure. Comments indicate spectra recorded at different positions within the sample chamber or after RXES measurements.

pressure (GPa)	$\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (%)	comment
0	12.53	
36	44.34	
61	25.42	off-center
61	48.87	center
61	48.60	center
69	52.54	
69	30.14	off-center
88	50.31	
88	35.13	off-center
88	53.41	center after RXES
88	38.58	off-center after RXES
102	56.07	
102	38.16	off-center

A.8.3 Comparison of XES spectra between analyzer crystal 1 and 2

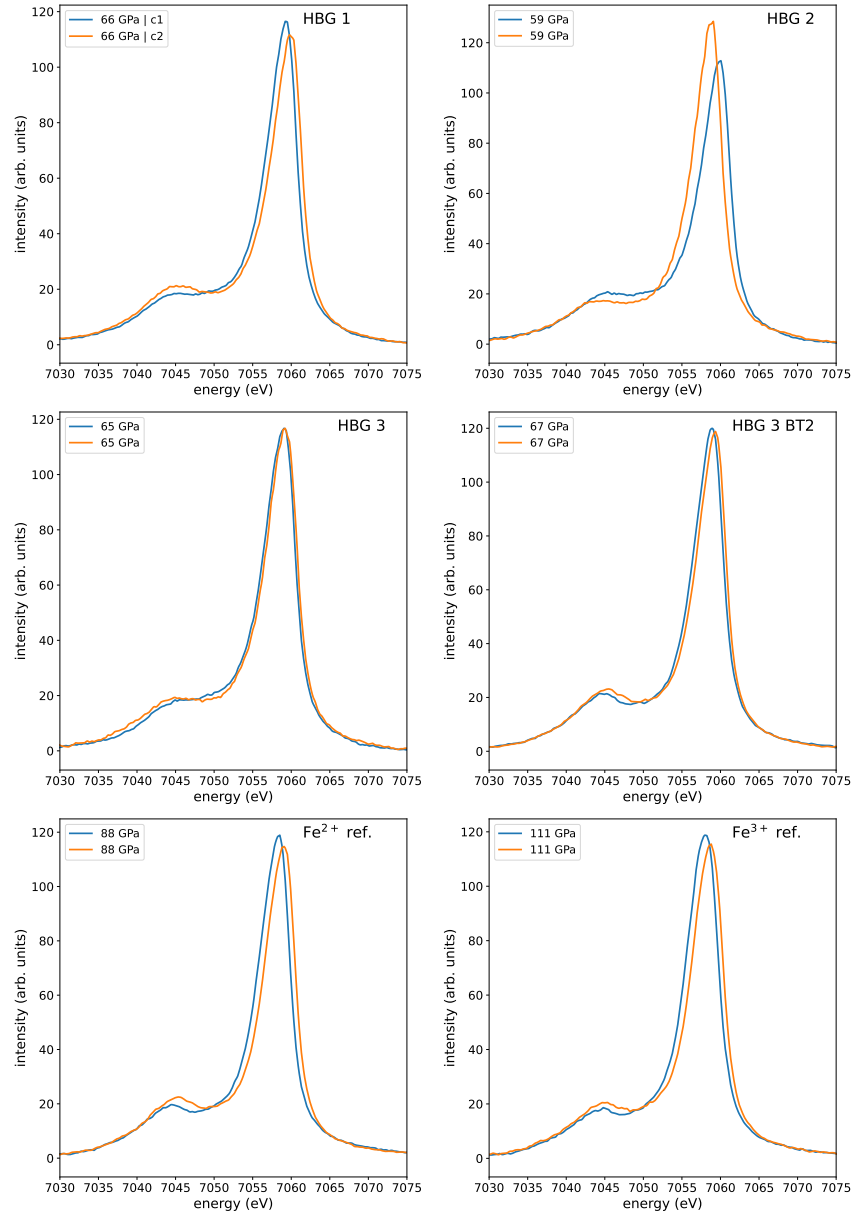


Figure A.38: XES spectra as a comparison between analyzer crystal 1 and crystal 2 for different samples. **Top left)** HBG 1, **top right)** HBG 2, **middle left)** HBG 3 first experiment, **middle right)** HBG 3 second experiment, **bottom left)** Fe^{2+} reference and **bottom right)** Fe^{3+} .

A.8.4 IAD value tables

Table A.13: IAD values as a function of pressure for two crystals of HBG 1.

pressure (GPa)	crystal 1 (IAD)	crystal 2 (IAD)
27	0.0762	0.1740
33	0.0723	0.1729
37	0.2466	0.1468
51	0.2105	0.0930
56	0.1733	0.1572
62	0.2327	0.1458
66	0.0961	0.2016
75	0.1915	0.1145
83	0.1517	0.1211
88	0.0838	0.0854
100	0.0507	0.1134
110	0.0762	0.0546
120	0.0000	0.0000

Table A.14: IAD values as a function of pressure for two crystals of HBG 2.

pressure (GPa)	crystal 1 (IAD)	crystal 2 (IAD)
18	0.1343	0.1045
23	0.3192	0.1432
28	0.3407	0.0905
33	0.3122	0.0943
39	0.3053	0.0934
49	0.3078	0.1362
58	0.2799	0.0798
59	0.2898	0.1073
66	0.1829	0.0774
70	0.1539	0.0805
78	0.0583	0.1359
85	0.1640	0.0837
98	0.1299	0.0887
109	0.0000	0.0000

Table A.15: IAD values as a function of pressure for two crystals of HBG 3.

pressure (GPa)	crystal 1 (IAD)	crystal 2 (IAD)
21	0.3202	0.0997
25	0.2437	0.1590
31	0.1926	0.1081
38	0.2453	0.0959
44	0.2774	0.0742
49	0.2976	0.0651
62	0.2134	0.0699
65	0.1260	0.0639
70	0.1543	0.0795
75	0.1809	0.0554
80	0.1315	0.0483
89	0.1265	0.0499
96	0.1529	0.0451
102	0.0816	0.0516
106	0.0574	0.0357
119	0.0000	0.0000

Table A.16: IAD values as a function of pressure for two crystals of HBG 3 (second experiment).

pressure (GPa)	crystal 1 (IAD)	crystal 2 (IAD)
11	0.2838	0.0916
20	0.2610	0.0766
29	0.2603	0.0702
40	0.2537	0.1384
49	0.1568	0.1168
57	0.1197	0.0898
67	0.1416	0.0852
78	0.0326	0.0554
85	0.0266	0.0294
95	0.0148	0.0196
104	0.0000	0.0000

Table A.17: IAD values as a function of pressure for two crystals of the Fe²⁺ reference.

pressure (GPa)	crystal 1 (IAD)	crystal 2 (IAD)
12	0.1894	0.1512
26	0.1659	0.0934
33	0.1161	0.0645
59	0.0831	0.0518
72	0.0572	0.0289
88	0.0269	0.0376
97	0.0263	0.0605
106	0.0181	0.0213
115	0.0000	0.0000

Table A.18: IAD values as a function of pressure for two crystals of the Fe³⁺ reference.

pressure (GPa)	crystal 1 (IAD)	crystal 2 (IAD)
10	0.3120	0.2992
20	0.3075	0.1237
31	0.2090	0.1296
40	0.1823	0.1307
50	0.1555	0.1059
60	0.0790	0.1283
66	0.1373	0.1239
79	0.1577	0.1193
88	0.0614	0.0759
98	0.0246	0.0394
111	0.0547	0.0179
118	0.0000	0.0000

A.8.5 M1 analysis tables and figure

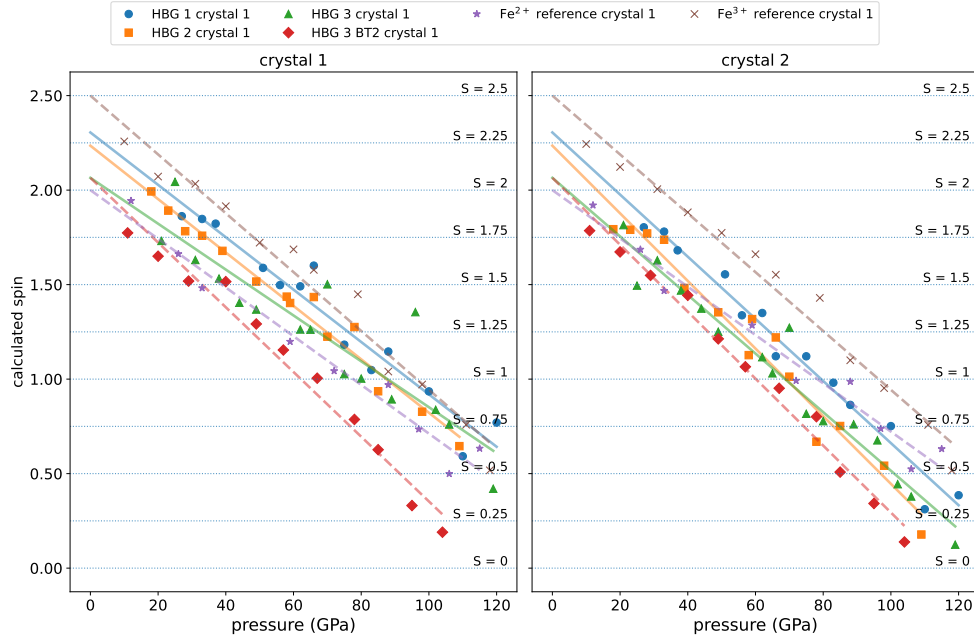


Figure A.39: Pressure-dependent calculated spin from M1 positions for all measured samples from two experiments based on M1 positions from different samples of varying oxidation and spin state published from Lafuerza et al. [28]. Results obtained via **left**) analyzer crystal and **right**) analyzer crystal two. The linear fit serves as a guide to the eye, where the solid line is used for the first experiment and the dashed line represent the second experiment.

Table A.19: Fe²⁺ reference: M1 positions in eV and their shifted M1 position and calculated spin for both analyzer crystals (c) at different pressures.

p (GPa)	M1 c1	M1 c2	sh. M1 c1	sh. M1 c2	spin c1	spin c2
12	7058.61	7058.95	7059.36	7059.34	1.94	1.92
26	7058.45	7058.81	7059.19	7059.20	1.66	1.69
33	7058.34	7058.68	7059.08	7059.07	1.48	1.47
59	7058.17	7058.57	7058.91	7058.96	1.20	1.28
72	7058.07	7058.40	7058.82	7058.79	1.04	0.99
88	7058.03	7058.39	7058.77	7058.78	0.97	0.99
97	7057.89	7058.24	7058.63	7058.63	0.74	0.74
106	7057.75	7058.11	7058.49	7058.50	0.50	0.52
115	7057.83	7058.18	7058.57	7058.57	0.63	0.63

Table A.20: Fe³⁺ reference: M1 positions and calculated spin for both analyzer crystals at different pressures.

p (GPa)	M1 c1	M1 c2	sh. M1 c1	sh. M1 c2	spin c1	spin c2
10	7058.73	7059.08	7059.52	7059.51	2.26	2.24
20	7058.61	7059.01	7059.41	7059.44	2.07	2.12
31	7058.59	7058.93	7059.38	7059.37	2.03	2.01
40	7058.52	7058.86	7059.31	7059.29	1.91	1.88
50	7058.40	7058.79	7059.19	7059.22	1.72	1.77
60	7058.38	7058.72	7059.17	7059.15	1.69	1.66
66	7058.31	7058.65	7059.10	7059.09	1.58	1.55
79	7058.23	7058.58	7059.02	7059.01	1.45	1.43
88	7057.98	7058.38	7058.77	7058.81	1.04	1.10
98	7057.94	7058.29	7058.73	7058.72	0.97	0.95
111	7057.81	7058.17	7058.60	7058.60	0.76	0.76
118	7057.66	7058.02	7058.45	7058.45	0.52	0.52

Table A.21: HBG 1: M1 positions and calculated spin for both analyzer crystals at different pressures.

p (GPa)	M1 c1	M1 c2	sh. M1 c1	sh. M1 c2	spin c1	spin c2
27	7059.31	7058.88	7059.29	7059.26	1.86	1.80
33	7059.30	7058.86	7059.28	7059.24	1.85	1.78
37	7059.29	7058.80	7059.27	7059.18	1.82	1.68
51	7059.14	7058.73	7059.12	7059.10	1.59	1.55
56	7059.09	7058.60	7059.07	7058.97	1.50	1.34
62	7059.09	7058.60	7059.06	7058.98	1.49	1.35
66	7059.15	7058.46	7059.13	7058.84	1.60	1.12
75	7058.90	7058.46	7058.88	7058.84	1.18	1.12
83	7058.82	7058.38	7058.80	7058.75	1.05	0.98
88	7058.88	7058.31	7058.85	7058.68	1.15	0.86
100	7058.75	7058.24	7058.73	7058.61	0.94	0.75
110	7058.54	7057.97	7058.52	7058.35	0.59	0.31
120	7058.65	7058.02	7058.63	7058.39	0.77	0.39

Table A.22: HBG 2: M1 positions and calculated spin for both analyzer crystals at different pressures.

p (GPa)	M1 c1	M1 c2	sh. M1 c1	sh. M1 c2	spin c1	spin c2
18	7059.45	7058.94	7059.37	7059.25	1.99	1.79
23	7059.39	7058.94	7059.31	7059.25	1.89	1.79
28	7059.32	7058.93	7059.25	7059.24	1.78	1.77
33	7059.31	7058.91	7059.23	7059.22	1.76	1.74
39	7059.26	7058.75	7059.18	7059.06	1.68	1.48
49	7059.16	7058.67	7059.09	7058.99	1.52	1.35
58	7059.11	7058.54	7059.04	7058.85	1.44	1.13
59	7059.09	7058.65	7059.02	7058.96	1.40	1.32
66	7059.11	7058.59	7059.04	7058.91	1.43	1.22
70	7058.98	7058.47	7058.91	7058.78	1.22	1.01
78	7059.01	7058.26	7058.94	7058.57	1.28	0.67
85	7058.81	7058.31	7058.73	7058.62	0.94	0.75
98	7058.74	7058.18	7058.67	7058.49	0.83	0.54
109	7058.63	7057.96	7058.56	7058.27	0.65	0.18

Table A.23: HBG 3: M1 positions and calculated spin for both analyzer crystals at different pressures.

p (GPa)	M1 c1	M1 c2	sh. M1 c1	sh. M1 c2	spin c1	spin c2
21	7059.23	7058.80	7059.23	7059.28	1.73	1.81
25	7059.42	7058.61	7059.41	7059.08	2.04	1.49
31	7059.17	7058.69	7059.16	7059.16	1.63	1.63
38	7059.11	7058.59	7059.11	7059.07	1.53	1.47
44	7059.04	7058.53	7059.03	7059.01	1.40	1.37
49	7059.02	7058.46	7059.01	7058.94	1.37	1.25
62	7058.95	7058.38	7058.94	7058.86	1.26	1.12
65	7058.95	7058.33	7058.94	7058.80	1.26	1.03
70	7059.10	7058.47	7059.09	7058.95	1.50	1.27
75	7058.81	7058.20	7058.80	7058.68	1.03	0.82
80	7058.80	7058.18	7058.79	7058.65	1.00	0.78
89	7058.73	7058.17	7058.72	7058.64	0.89	0.76
96	7059.01	7058.11	7059.00	7058.59	1.35	0.68
102	7058.70	7057.97	7058.69	7058.45	0.84	0.44
106	7058.65	7057.94	7058.64	7058.41	0.76	0.38
119	7058.44	7057.78	7058.44	7058.26	0.42	0.12

Table A.24: HBG 3 BT2: M1 positions and calculated spin for both analyzer crystals at different pressures.

p (GPa)	M1 c1	M1 c2	sh. M1 c1	sh. M1 c2	spin c1	spin c2
11	7058.62	7059.02	7059.25	7059.26	1.77	1.79
20	7058.54	7058.96	7059.18	7059.19	1.65	1.67
29	7058.46	7058.88	7059.10	7059.12	1.52	1.55
40	7058.46	7058.82	7059.10	7059.05	1.52	1.44
49	7058.33	7058.68	7058.96	7058.91	1.29	1.21
57	7058.24	7058.59	7058.88	7058.82	1.15	1.07
67	7058.15	7058.52	7058.79	7058.76	1.00	0.95
78	7058.02	7058.43	7058.66	7058.67	0.79	0.80
85	7057.93	7058.26	7058.56	7058.49	0.63	0.51
95	7057.75	7058.16	7058.38	7058.39	0.33	0.34
104	7057.66	7058.03	7058.30	7058.27	0.19	0.14

List of Acronyms

BA	Boehler-Almax diamond
BIF	banded iron formation
BO	bridging oxygen
BSE	bulk silicate earth
CEE	constant emission energy
CFT	crystal field theory
CIE	constant incident energy
CMB	core-mantle-boundary
CMS	center of mass
DAC	diamond anvil cell
DESY	Deutsches-Elektronen-Synchrotron
EDX	energy dispersive X-ray spectroscopy
EFG	electric field gradient
EOS	equation of state
EPMA	electron probe microanalysis
ESRF	European Synchrotron Radiation Facility
EXAFS	extended X-ray absorption fine structure
Fe	iron
FMQ	fayalite-magnetite-quartz buffer
HBG	haplobasaltic glass
HERFD-XANES	high-energy-resolution fluorescence-detected X-ray absorption near-edge structure spectroscopy
HP	high pressure
HP/HT	high pressure and high temperature
HS	high-spin
HT	high temperature
IAD	integral of absolute difference
IRO	intermediate-range order
IW	iron-wüstite buffer
LS	low-spin
LVZ	low velocity zone
M1	first moment
MD	miniature diamond
MH	magnetite-hematite buffer
MOCT	metal-oxygen charge transfer
MORB	mid-ocean ridge basalt
NBO	non-bridging oxygen
NBO/T	non-bridging oxygen per tetrahedra
NFS	nuclear forward scattering
NIST	National Institute of Standards and Technology
NNO	nickel-nickel oxide buffer
ppuc	polyhedra per unit cell

PREM	Preliminary Reference Earth Model
ROI	region-of-interest
RXES	resonant X-ray emission spectroscopy
SEM	scanning electron microscope
SMS	synchrotron Mössbauer spectroscopy
SRO	short-range order
ST	standard diamond
ULVZ	ultra-low velocity zone
vtc	valence-to-core
WCCA	wet-chemical colorimetric analysis
XES	X-ray emission spectroscopy
XRD	X-ray diffraction

List of publications and conference contributions

Publications as co-author

- L. Friedrich, M. Požar, A. Perera, M. Paulus, **N. Thiering**, J. Savelkouls, E. Schneider, B. Lovrinčević, D. Lützenkirchen-Hecht, C. Sternemann, Molecular Microheterogeneity: Structure Formation in Amine-Water Mixtures, JACS, doi.org/10.1021/jacs.5c17604 (2026).
- Mi. Moron, S. Dogan-Surmeier, Ma. Moron, **N. Thiering**, M. Paulus, C. Sternemann, M. Tolan, B. Murphy, V. Honkimäki, J. Nase, A high-pressure/high-temperature cell for interface-sensitive X-ray scattering experiments of supercritical fluids; Encyclopedia of Solid-Liquid Interfaces, 400-408, doi.org/10.1016/B978-0-323-85669-0.00104-5 (2024).
- J.M. Kaa, Z. Konôpková, T.R. Preston, V. Cerantola, C.J. Sahle, M. Förster, C. Albers, L. Libon, R. Sakrowski, L. Wollenweber, K. Buakor, A. Dwivedi, M. Mishchenko, M. Nakatsutsumi, C. Plückthun, J.-P. Schwinkendorf, G. Spiekermann, **N. Thiering**, S. Petitgirard, M. Tolan, M. Wilke, U. Zastrau, K. Appel and C. Sternemann, A von Hámos spectrometer for diamond anvil cell experiments at the High Energy Density Instrument of the European X-ray Free-Electron Laser, Journal of Synchrotron Radiation 30, 822, doi.org/10.1107/S1600577523003041 (2023).
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Conference contributions as presenting author

- AIRAPT Matsuyama – "Investigating *in situ* the electronic structure and spin state of iron in Fe_2O_3 at high pressure and temperature conditions of the Earth's lower mantle", poster (2025)
- Seminar Beschleunigerphysik und Synchrotronstrahlung, Anwendungen in der Festkörperphysik – " *In situ* study of Fe_2O_3 at pressure and temperature conditions of the Earth's lower mantle", talk (2024)
- EHPRG and AIRAPT Edinburgh (The European High Pressure Research Group and International Association for the Advancement of High Pressure Science and Technology) – " *In situ* study of Fe_2O_3 at pressure and temperature conditions of the Earth's lower mantle", poster (2023)
- DESY User Meeting – "X-ray emission setup at P01 to study the electronic structure of iron bearing compounds *in situ* at high pressure and high temperature", poster (2023)
- DPG Regensburg – "X-ray emission spectroscopy at DELTA", poster (2022)
- DPG Regensburg – "X-ray emission setup to study the electronic structure of iron bearing compounds *in situ* at high pressure and high temperature", poster (2022)
- GeoMinKöln – "X-ray emission setup to study the electronic structure of iron bearing compounds *in situ* at high pressure and high temperature", poster (2022)
- DPG (virtual conference) (Deutsche Physikalische Gesellschaft e.V., Germany) – "X-ray emission spectroscopy setup at DELTA", poster (2021)

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