

Using 4D synchrotron X-ray microtomography rigs for time-resolved X-ray diffraction experiments: applications with the Mjölñir suite

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Synopsis:

High-energy synchrotron X-ray diffraction can be performed through miniature triaxial microtomography rigs, enabling time-resolved phase tracking, strain and stress measurements during *in situ* experiments on representative sample volumes.

Abstract:

Synchrotron 4D X-ray microtomography provides unique insights into evolving microstructures during deformation, fluid flow and mineral transformations, but offers limited access to crystallographic information such as phase composition, lattice strain, and stress. Conversely, synchrotron X-ray diffraction (XRD) provides direct crystallographic measurements but is commonly restricted to small sample volumes and specialised sample environments. Here, we demonstrate the use of the Mjölñir and Heitt Mjölñir miniature triaxial deformation rigs, originally developed for 4D synchrotron microtomography, as platforms for time-resolved high-energy XRD experiments. Using experiments performed at beamline I15 (Diamond Light Source) supported by theoretical analysis, we evaluate diffraction contributions from pressure vessels and ancillary components, establish practical beamline setup and acquisition procedures, and assess controls on diffraction quality. We show that high-quality diffraction data can be acquired through X-ray-transparent pressure vessels, enabling phase identification, reaction tracking and lattice-strain measurements in representative sample volumes of geological materials. The rotational symmetry of the rigs further enables rocking, sweeping and mapping acquisition strategies, improving powder statistics while preserving realistic sample geometries and boundary conditions. These results provide a practical framework for integrating XRD with synchrotron microtomography and open new opportunities for linking crystallographic evolution to four-dimensional microstructural evolution during *in situ* experiments.

Keywords: Synchrotron X-ray diffraction; Synchrotron X-ray microtomography; experimental geosciences;

1. Introduction:

Synchrotron-based four-dimensional (3D + time) X-ray microtomography (4D μ CT) has become a key experimental approach for investigating the evolution of microstructure in materials subjected to coupled thermal, hydraulic and mechanical conditions. Recent developments in X-ray transparent flow cells, uniaxial and triaxial deformation rigs have enabled *in situ* imaging of millimetre to centimetre-scale samples under controlled stress states and elevated temperatures, thus allowing experiments on geometries and volumes that remain representative of heterogeneous natural and engineered materials (Fusseis et al. 2014).

Among the growing number of such experimental platforms (see Noiriél and Renard (2022, Freitas et al., (2024) and Shahin et al., (2026) for extensive listing), the Mjölñir suite, including Sleipnir (Fusseis et al., 2014), Mjölñir (Butler et al., 2020), Storr Mjölñir (Cartwright-Taylor et al., 2022) and Heitt Mjölñir (Freitas et al., 2024), was specifically designed to combine mechanical robustness, rotational symmetry and relatively high X-ray transparency for 3rd and 4th generation synchrotron light sources. This design philosophy enables 4D microtomography studies at high spatial (>100 nm) and temporal resolution ($<s$) while accessing pressure–temperature conditions relevant to crustal and near-surface geosystems. These rigs have been deployed across several international synchrotron radiation facilities, national UK facilities (NXCT), and laboratory sources and have demonstrated the capacity for

near-continuous four-dimensional imaging of dynamic processes. Synchrotron μ CT studies using these devices have provided direct access to the spatio-temporal evolution of porosity, fractures, reaction, fluid pathways and mineral textures during deformation and mineral transformation experiments. Applications include brittle failure, pressure-solution, multiphase fluid flow, dehydration–rehydration reactions and fluid–rock interactions (Cartwright-Taylor et al. 2022, Renard et al. 2004; Thaysen et al. 2023; Gilgannon et al. 2023, Freitas et al. 2024, as examples) enabling quantitative tracking of microstructural changes in four dimensions. Owing to their open-design philosophy, these rigs have been adopted by an expanding user community and are now supporting an increasing number of studies across geoscience and materials-science applications (Butler et al. 2020; Freitas et al. 2024, Shahin et al. 2026).

Despite these advances, synchrotron 4D μ CT suffers from intrinsic limitations (Withers et al. 2021). First, phase discrimination relies mainly on X-ray attenuation contrast, which can be insufficient when phases have similar compositions or densities. This strongly affects multiphase systems composed of minerals with comparable effective atomic numbers, as well as solid–solid transformations involving limited density contrast, a particularly frequent problem with silicates (Chauhan et al. 2016; Rizzo et al., 2024). Even in systems with intrinsically strong density contrasts, complex phase geometries, fine-scale intergrowths or crystallographic intertwining can prevent reliable phase segmentation (Mayo et al. 2012, Chauhan et al. 2016). Second, the spatial and temporal resolution is limited by experimental constraints such as detector size, optical elements, and the quality of data acquisition. Depending on the nature and speed of the processes under investigation this often necessitates compromise between spatial resolution, image quality and temporal resolution. This spatial-temporal trade-off limits the early detection of reactions, phase transitions, deformation localisation and fracture nucleation, which commonly initiate below the resolution accessible to high-energy imaging beamlines. Processes occurring below the accessible spatial or temporal resolution therefore remain undetected during the experiment. Third, and more fundamentally, absorption and phase-based μ CT provides little direct information on lattice-scale properties of the investigated materials. Variations in lattice parameters, elastic strain, residual stress and lattice preferred orientation (LPO) cannot be directly quantified, despite their fundamental importance in governing reaction kinetics, deformation mechanisms and stress redistribution during mineral transformations and rock deformation (e.g. Powell et al., 2017; Wheeler et al., 2020).

In contrast, X-ray diffraction (XRD) techniques are well established for probing crystallographic structure, phase composition, lattice parameters and elastic strain (Young 1993, Cullity and Stock 2014, Chen et al. 2021, Oddershede et al. 2010). Time-resolved synchrotron XRD has been extensively used to track phase transformations and quantify stress evolution during *in situ* experiments (Shrank et al. 2020; Chen et al. 2021). These approaches have been particularly successful in high-pressure and high-temperature studies focusing on lattice-scale processes and elastic or plastic deformation mechanisms (e.g. Chen et al., 2021; Zhang et al., 2024). However, these experiments are typically conducted on millimetre- to sub-millimetre-scale samples using apparatus optimised for diffraction rather than imaging (DAC, Paris Edinburg Cells, apparatus with transparent windows, multi anvils, etc.) (King et al. 2016, Vaughan et al. 2020). This focus on small, idealised samples imposes important limitations. First, the representativity of the tested volume is reduced when dealing with heterogeneous materials such as rocks, concretes or granular aggregates. Second, conventional XRD experiments are largely microstructure-agnostic: while they provide precise crystallographic information averaged over the illuminated volume, they do not capture the

evolving three-dimensional architecture of the sample, including porosity, grain contacts and reaction-induced damage. As a result, linking lattice-scale strain and stress to microstructural evolution remains challenging while proven critical with larger sample volumes techniques.

Bridging the gap between 4D microtomography and time-resolved XRD therefore represents a major methodological opportunity because the techniques provide inherently complementary information, spanning length scales from the crystal lattice to centimetre-sized samples and timescales from sub-second processes to experiments lasting several days. It is thus particularly important to establish if these complementary techniques can be sequentially or simultaneously combined on the same sample. While several beamlines now offer combined diffraction and imaging capabilities, such as PSICHÉ at SOLEIL (King et al., 2016; Boulard et al., 2018), K11-DIAD (Reinhard et al., 2021) and I12-JEEP (Drakopoulos et al. 2015) at Diamond Light Source, MAXPD (Whitaker et al. 2018) at NSLS-II, and the COMPRES/GSECAR beamlines at the APS (Rivers et al. 1998) (non-exhaustive list), these approaches have not yet been applied to hydraulic deformation apparatus (triaxial type). This may result from intrinsic design and setup limitations such as beamline geometry, beam type (energy, flux etc.). However, even in the favourable cases, existing implementations often rely on solid pressure media, large-volume presses (e.g. UToPEC or RotoPEC, King et al. 2016) or bespoke uniaxial devices, which differ substantially from the sample environments typically used in synchrotron 4D μ CT deformation studies.

The latest generation of X-ray transparent triaxial rigs developed for synchrotron microtomography, such as the Mjölñir suite, provides a model experimental platform for such integration. Their compatibility with high-energy monochromatic and filtered white synchrotron beams makes them suitable not only for transmission imaging but also for spatially and temporally resolved XRD measurements. Their rotational symmetry, originally developed to enable tomographic acquisition through beam transmission, is a distinct feature compared to “window”-based equipment and provides both challenges and opportunities for new and complex experimental strategies and protocols. The ultimate goal of such developments is to enable stress-strain analysis, orientation distribution and ultimately diffraction tomography (Jacob et al. 2025). While such developments are currently happening in parallel at the various facilities and using a large pool of different apparatus, there is still no comprehensive guide on how to use axis-symmetric X-ray transmission deformation devices initially designed for tomographic studies for XRD acquisition at high energy beamlines as well as a critical discussion of the associated benefits and limitations.

In this paper, we demonstrate the feasibility and potential of using 4D synchrotron microtomography rigs for time-resolved X-ray diffraction experiments at high-energy diffraction beamlines. Using the Mjölñir and Heitt Mjölñir rigs as examples, we present a proof-of-concept study conducted at the I15 beamline at Diamond Light Source. This study first demonstrates the intrinsic XRD compatibility of these devices, then provides theoretical and practical guidelines for optimising beamline setup and acquisition strategies within this experimental geometry, and finally illustrates, through selected examples, the complementarity between XRD and microtomographic measurements. We show that lattice-scale information can be retrieved through the pressure vessels with sufficient quality to enable phase identification/mapping and stress analysis, opening new perspectives for fully coupled microstructural and crystallographic studies during *in situ* deformation and mineral transformation experiments. We aim for this paper to provide an extensive practical guide for the design, setup and operation of future diffraction experiments using axis-symmetric synchrotron deformation apparatus. Beyond demonstrating feasibility, the approach offers a

common experimental framework that facilitates direct comparison between imaging and diffraction measurements under identical boundary conditions, benefiting the growing user community already employing these devices for 4D microtomography studies.

2. Beamline and rig setup at high-energy diffraction beamlines

This section details the diffraction beamline configuration, the installation and use of miniature triaxial rigs at a diffraction beamline, the different rig and sample configurations tested, and the acquisition strategies explored. It is intended as a step-by-step methodological guide to enable X-ray diffraction (XRD) experiments using tomography-oriented deformation devices of similar design. The section is designed both for end-users and beamline scientists, as such apparatuses are typically hosted at universities and visiting laboratories rather than being permanently installed at synchrotron facilities.

2.1 Beamline setup and calibration

A) Beamline setup:

These proof-of-concept XRD measurements were carried out at the I15 beamline at Diamond Light Source. The Diamond Light Source storage ring operates with an electron beam energy of 3 GeV and a beam current of ~300 mA (~250 mA for NT40566, 275-300 mA for CY40439). The beamline was configured in its high-energy mode, using a monochromatic X-ray beam with an energy of 72 keV, generated by a 3.5 T superconducting multipole wiggler and monochromated by a Si (111) double crystal monochromator. This high energy is critical to ensure sufficient penetration through pressure vessels and sample assemblies. At the sample position, the incident beam size was approximately 120 μm (H) $\times$ 80 μm (V), focused by Kirkpatrick-Baez mirrors. No further beam shaping optics or filters were employed. After the beam exits the vacuum beam pipe via a diamond window in the experimental hutch, a pair of clean-up slits and a tungsten collimator (just before the sample stage) reduce air/side scatter from along the beam path. A 3 mm diameter tungsten beam stop was positioned downstream of the sample to protect the detector from the direct (forward scattered) beam.

The sample stage arrangement is typical of diamond anvil cell extreme conditions beamlines. It consists of a rotation stage on top of which are three (x,y,z) translation stages. This whole assembly is mounted on a Newport diffractometer base which can rotate, tilt and translate perpendicular to the beam. At a given point above the rotation stage the rotation centre is determined, and this is then aligned to the beam. The x,y,z translation stages on top of the rotation stage then allow the sample to be brought to the centre of rotation/beam position. A silicon photodiode positioned behind the sample is used for alignment via absorption contrast.

The rotation stage can rotate through 360° (not continuously), with resolution < 0.1 degree, the translation stages have a travel range of 25 mm, with 1 μm resolution. To ensure that the vertical translation stage is always able to scan the entirety of the sample's vertical dimension through the beam, tripods of differing heights, mounted on top of the sample stage stack, are used to compensate for the individual rigs' differing height requirements. Diffraction data were collected using a Pilatus3X CdTe 2M detector (pixels 172 $\times$ 172 μm). The detector can run at a maximum rate of 250 Hz, and the readout time is 1 ms.

B) Sample alignment

Sample alignment is relatively straightforward using the configuration described above. The sample (or calibration standard) is positioned at the intersection of the incident beam and the rotation axis, which are pre-aligned during beamline setup. Alignment is performed using absorption-contrast scans acquired while translating the sample through the beam along the

two horizontal translation axes (x and y). For each scan, the stage is rotated such that the translation direction is orthogonal to the beam path. The resulting transmission profiles allow the geometric centre of the sample to be identified and aligned with both the beam position and the rotation axis.

Accurate centring is particularly important for rotational acquisition protocols. Misalignment can affect the diffraction geometry and introduce artefacts that become more significant during rocking, sweeping and mapping acquisitions. The implications of sample misalignment for beam path length, illuminated volume and peak broadening are discussed in later sections. Consequently, precise alignment constitutes a critical preparatory step prior to diffraction data acquisition.

C) Detector calibration:

Detector calibration for powder diffraction experiments is both for the sample to detector distance and for determining the geometric centre of the 2D detector area as well as pitch and yaw with respect to the incoming x-ray beam. In the present experiments calibration was performed using CeO₂ and LaB₆ NIST powder standards. For both rigs, calibration was achieved using a standard jacketed CeO₂ or LaB₆ powder sample (~3.2 mm thick) positioned at the geometric centre of the rig, using an exposure time of 5 s and without the pressure vessel.

2.2 Miniature triaxial device installation

Experiments were conducted using the Mjölñir and Heitt Mjölñir miniature triaxial deformation rigs, originally developed for synchrotron 4D microtomography (Butler et al., 2020; Freitas et al., 2024). Both devices employ X-ray-transparent pressure vessels compatible with high-energy monochromatic and filtered white-beam experiments and allow deformation under controlled confining pressure, axial load, pore fluid pressure and temperature.

The rigs accommodate cylindrical samples of approximately 3.2 mm × 10 mm (diameter × length) in Mjölñir and 10 mm × 20 mm in Heitt Mjölñir. These dimensions are substantially larger than those commonly used in high-pressure synchrotron XRD experiments and are representative of many imaging-based deformation apparatuses. A key feature for the present study is the rotational symmetry of the rigs, allowing continuous sample rotation through 360°. Although originally designed for tomographic acquisition, this capability is exploited here for XRD acquisition strategies (Section 2.4).

Installation at beamline I15 is straightforward. Each rig is mounted on an aluminium dish attached to a Thorlabs MB1015/M optical breadboard, which is secured to the kinematic sample stage via a custom mounting plate. For Mjölñir, 65 mm table legs place the sample within the full 25 mm vertical travel range of the experimental stage, simplifying beam alignment. Heitt Mjölñir requires shorter 46 mm table legs and more careful vertical adjustment because of its larger sample length (20 mm).

Compared with typical microtomography beamlines, diffraction beamlines such as I15 have a higher density of beamline components in the immediate vicinity of the sample. This reduces the available clearance around the deformation rig and imposes additional constraints on cable management and rig access (Figure 1).

Peripheral equipment, including high-pressure pumps, LVDTs, valves, heating systems and fluid tubing, was installed following the procedures described by Freitas et al. (2024). The compact pump system proved advantageous in the confined beamline environment, while flexible 1/16" PEEK capillaries facilitated stage rotation and simplified cable and tubing management.

3. Diffraction analysis through Mjöltnir and Heitt Mjöltnir rigs and components

3.1 Diffraction contributions from rig components

For each apparatus, we systematically tested the pressure vessel materials and wall thicknesses, sample jackets and baffling materials (thermal insulation) as well as various sample types (metals and geological materials). Having a suite of tested materials is critical for designing the experiments (see sections 3.1D and 3.2E) and ensuring the compatibility between the target pressure, temperature and acquisition conditions, and the nature of the selected samples.

One of the key advantages of bespoke miniature rigs such as the Mjöltnir suite is the ability to use multiple pressure vessel materials depending on experimental requirements. Original designs employed aluminium vessels, offering a favourable compromise between mechanical strength and X-ray attenuation (Freitas et al. 2024). Other materials can be used, such as carbon fibre composite (CF), PEEK, CF loaded PEEK for low-pressure or low-temperature experiments, and titanium for higher pressure and temperature conditions (Freitas et al. 2025).

For X-ray imaging, vessel selection is primarily governed by elemental composition and density, which control X-ray transmission, beam type selection (mono vs polychromatic, beam size, flux, filters etc.), image contrast and exposure time. In XRD experiments, however, the pressure vessel contributes directly to the measured diffraction signal. Consequently, in addition to transmission characteristics, the crystallographic signature (symmetry, peak positions etc.) of the vessel material relative to that of the sample becomes essential. The main risk resides in the potential overlap between diffraction peaks from the vessel and those of the sample, which can hinder both qualitative and quantitative analysis or would imply complex post-processing and deconvolution steps. Vessel materials should therefore be selected to minimise peak overlap, ideally by choosing crystallographic systems with distinct symmetries and peak positions relative to the sample phases. This requires prior knowledge of both beamline characteristics (wavelength), sample mineralogy and vessel/parts on the beam path diffraction, which can be acquired via preliminary tests or numerical simulations tailored to the target beamline characteristics (beam type, optical elements, distances, detector, etc).

Knowing the vessel materials and beamline characteristics, it is possible to predict positions of the vessel peaks from classical CIF files and open software like GSAS-II (Toby & Von Dreele, 2013) or Dioptas (Prescher & Prakapenka, 2015). This prediction must, however, account for the axisymmetric geometry of cylindrical pressure vessels. Owing to this geometry, diffraction originates from both the upstream vessel wall and the downstream vessel wall, producing a characteristic pattern composed of two identical series of reflections. These reflections arise from different apparent diffraction centres and therefore exhibit different apparent sample-to-detector distances (SDD). Consequently, each vessel reflection appears as a doublet in the measured diffraction pattern. The upstream vessel wall, which possesses the larger apparent SDD, generates Debye-Scherrer rings at slightly larger 2θ values than the sample, whereas the downstream vessel wall generates reflections at smaller 2θ values.

Using the crystallographic information of the vessel material together with the vessel geometry from the CAD models of the vessels given in Butler et al. (2020) and Freitas et al. (2024), the position of the apparent diffraction centre for each vessel wall can be estimated geometrically (Figure 2). The apparent diffraction centre of each vessel wall is assumed to lie at the centre of mass of the annular wall section intersected by the beam and is calculated as:

$$\delta D = IR \pm \frac{(OR-IR)}{2} \quad (1)$$

With IR and OR being the inner and outer radii of the tube/vessel, respectively. For Mjölñir, the shift from sample centre is -4.5 mm and +4.5 mm for the upstream wall and the downstream wall, respectively (using the thinner vessel used in Gilgannon et al, 2023.; and ± 5.5 mm for standard Mjölñir vessel). In Heitt Mjölñir, the vessel dimensions being greater, the theoretical offset is expected to be ± 13 mm. This simple model has been used to predict aluminium vessel peaks for the Mjölñir rig (see figure 2) and compared against our measurements (reported in figure 3).

From this, the predicted position of a ring based on a GSAS/Dioptas simulation at the SSD (corresponding to the sample centre) can be offset to simulate the pattern for the inner wall and outer wall using (see figure 2, for geometrical detail):

$$\varphi = \left(\frac{(D + \delta D) \tan \tan 2\theta}{D} \right) \quad (2)$$

Where φ is the new 2θ angle adjusted to convert a pattern position prediction at a sample to detector distance of D to a distance of $D + \delta D$. These calculated values were used to model the aluminium vessel diffraction pattern shown in Figure 2 and exhibit good agreement with the measured data.

Accurate centring of the rig is essential for rotational diffraction experiments (Section 2.1B). Misalignment alters the beam path through the pressure vessel, producing variations in the position and width of vessel-derived reflections during rotation. This enlarges the vessel diffraction footprint in 2θ space, reduces overlap-free regions available for sample identification, and becomes particularly significant during mapping acquisitions where the crossed vessel thickness varies across the sample (Figure S2).

A) Pressure vessels

Metal-alloy (aluminium and titanium) vessels produced sharp, intense and well-defined diffraction peaks in the measured patterns (Figure 3). We found that exposure times as short as 1 s were sufficient to obtain high-quality diffraction patterns from Mjölñir vessels. A 1 s exposure was also possible for Heitt Mjölñir vessels; however, because of their greater wall thickness and, in the case of titanium, higher material density, a minimum exposure time of 5 s was generally preferred.

One of the key features of these measurements is the presence of doublets for each diffraction peak, arising from diffraction through both the upstream and downstream vessel walls (Figures 2 and 3). The cubic and hexagonal crystal structures of the metallic alloys generate a relatively small number of reflections, even when accounting for the doublet features, thereby leaving large low- 2θ regions free of interference from vessel peaks. These reflections were readily identified in Dioptas using reference CIF files (Figure 3).

For aluminium alloys, no significant differences in diffraction peak positions were observed between the two alloys investigated (6062 and 7068). The principal reflections correspond to the (111), (200), (311) and (222) planes, producing peak doublets centred at approximately $2\theta = 4.2^\circ$, 4.8° , 6.8° and 8.1° , respectively (Figure 3) in agreement with published diffraction patterns. (Anghelina et al. 2017). These measurements were obtained using Mjölñir vessels, with alloy 6062 representing the standard vessel configuration (4 mm wall thickness) and grade 7068 with a reduced-thickness design (3 mm wall thickness) (see design given in Gilgannon et al. 2023). For Heitt Mjölñir, the aluminium diffraction pattern is identical to that described above (grade 7068); however, the larger vessel dimensions result in a greater separation of the peak doublets due to the increased distance between the upstream and downstream vessel walls.

Grade 5 titanium alloy produced a substantially more complex diffraction pattern than aluminium. The principal reflections form a dense population of peak doublets between 3.7° and 4.5° 2θ , dominated by the (100) and (101) reflections. A second cluster of smaller but regularly spaced doublets occurs between 5.7° and 8.3° 2θ and corresponds primarily to the (102), (110), (103) and (201) reflections (Figure 3) (Zhang et al. 2014).

PEEK vessels, being semicrystalline, generated broader low-angle diffraction features consisting of diffuse scattering superimposed on weak diffraction peaks (Figure 3). The principal broad diffraction feature extends from approximately 0 to 6° 2θ and contains four characteristic reflections, indexed as (100), (111), (200) and (211), centred at approximately 2.1° , 2.3° , 2.5° and 3.2° , respectively. At higher diffraction angles, the pattern is comparatively featureless, apart from a second broad region extending from approximately 7.5° to 10° 2θ .

In contrast to the sharp diffraction signatures produced by metallic vessels, PEEK vessels did not exhibit clearly resolved doublets. Instead, the diffraction contributions from the two vessel walls appeared to merge into broader composite peaks. Only subtle differences were observed between the two PEEK grades investigated (PEEK 1000 and PEEK 450GF), both of which produced very similar diffraction patterns. The principal distinction was a slightly elevated semicrystalline background in the PEEK 450GF material, attributable to the presence of glass fibres. This observation suggests that the crystallographic structure of the polymer dominates its diffraction behaviour, while relatively minor compositional differences between grades exert only a limited influence, consistent with previous studies (Wang et al. 2018; Bastan 2020).

Although the PEEK peaks appear prominent in the normalised intensity plots, their absolute diffracted intensity is significantly lower than that of the metallic vessels. Consequently, vessel selection should not be based solely on peak positions and diffraction-pattern appearance. Transmission characteristics and absolute diffracted intensity must also be considered, as these factors directly influence the quality of the diffraction data obtained from the sample.

B) Other components in the beam path (jackets and baffles)

All components intersecting the beam path contribute to both diffraction and attenuation. Consequently, in addition to the pressure vessel itself, it is important to evaluate the influence of common sample jackets, confining fluids and ancillary components such as thermal baffles, as each contributes additional diffraction features and reduces the 2θ space available for sample reflections.

For the low-temperature configurations of both devices, silicone jackets and polyolefin heat-shrink materials are commonly used because of their simplicity, reliability and cost-effectiveness (Freitas et al., 2024). Silicone tubing produced a detectable diffraction signal, although with extremely low intensity (243 counts s^{-1} compared to >3000 for other components, see figure 4). The pattern consisted of two broad low-angle peaks centred at 1.35° and 2.37° 2θ , together with a diffuse background contribution extending approximately from 0° to 9° 2θ .

In contrast, no measurable diffraction signal attributable to the confining fluids (water or silicone oil) was observed at 72 keV. Blank measurements acquired with these fluids produced no detectable diffraction features within the sensitivity limits of the present experimental configuration and are therefore not reported in Figure 4.

For high-temperature experiments using Heitt Mjölñir, PEEK baffles are employed to thermally isolate the aluminium pressure vessel from the heated sample assembly. The baffles (21 mm outer diameter, 15 mm inner diameter) generated diffraction patterns comparable to

those observed for the PEEK vessels described above. The diffraction peak positions were identical, and despite the cylindrical geometry of the component, no clearly resolved peak doublets were observed. The overall diffracted intensity was considerably lower than that of titanium vessels, indicating that the contribution of the baffles to the total pattern is relatively minor. Nevertheless, the broad diffuse scattering associated with the PEEK material can locally degrade background quality and may complicate identification or fitting of weak sample reflections occurring within the same angular range.

In the high-temperature configuration of Heitt Mjölñir, silicone jackets are replaced by thin copper jackets with a wall thickness of approximately 200 μm . The diffraction pattern of copper resembles those of the metallic pressure vessels, producing sharp and well-defined reflections. The principal peaks correspond to the (111), (200), (220), (311) and (222) planes and are located at approximately 4.8° , 5.5° , 7.7° and 9 to 9.5° 2θ , respectively matching typical copper XRD patterns (Phul et al. 2018). These reflections are sufficiently intense and well defined that they must be considered during experiment design and phase identification.

Finally, we also characterised the diffraction signal generated by the titanium piston used in Heitt Mjölñir, as well as the titanium piston tip employed in Mjölñir experiments involving pore-fluid pressure (Gilgannon et al., 2023). These components may contribute to the measured diffraction pattern when analyses are performed close to the sample–piston interface. The diffraction peaks are similar to those observed for the titanium pressure vessels; however, no peak doublets were observed. This behaviour is likely related to the much smaller central pore-fluid channel, approximately 1 mm in diameter for Heitt Mjölñir and 0.4 mm for the 3.2 mm Mjölñir configuration, which reduces the spatial separation between the effective diffraction centres and thus suppresses the doublet signature observed in the pressure vessels.

C) “Representative” suite of samples

Having identified the regions of reciprocal space unaffected by diffraction from the pressure vessels and ancillary rig components, we report here the XRD pattern for a range of representative geological materials under identical experimental conditions. The objective was to identify potential peak overlap between sample phases and rig-derived diffraction signals. The selected materials are representative of those routinely used in rock deformation, fluid–rock interaction and mineral transformation experiments conducted with the Mjölñir suite.

The investigated materials span the principal mineral groups commonly encountered in geological systems, including silicates, carbonates and sulfates. Silicate-rich samples comprised Clashach sandstone, dominated by quartz, and Mercia Mudstone Group (MMG) material, containing quartz, feldspars and clay minerals. Carbonate samples included South-East UK chalk and Carrara marble, while sulfate-bearing materials were represented by Volterra alabaster, composed predominantly of gypsum. In addition to evaluating peak overlap with rig components, these measurements provide insight into the influence of mineralogical complexity and grain size on diffraction quality, both of which represent important challenges when working with naturally heterogeneous geomaterials (see Section 5).

Samples typically measured 3.2 mm in diameter and 10 mm in length in the Mjölñir configuration, and 10 mm in diameter by 20 mm in the Heitt Mjölñir configuration. In general, geological materials produced considerably more complex diffraction patterns than the rig components owing to the lower symmetry and multiphase nature of common rock-forming minerals and geological materials.

The carbonate samples, chalk and Carrara marble, produced very similar diffraction patterns dominated by calcite reflections, with the principal peaks concentrated between

approximately 2° and 5° 2θ (Figure 5) and matching rhombohedral calcite structure (space group R-3c). In contrast, the sulfate sample exhibited a more complex pattern containing numerous closely spaced reflections, which may be challenging to isolate individually. Nevertheless, gypsum displays several distinctive low-angle reflections, notably the (020) and ($2\bar{2}1$) peaks at approximately 1.3° and 2.3° 2θ , respectively, which provide clear phase identification.

The silicate samples also generated complex diffraction patterns due to their mixed mineralogical composition. Clashach sandstone is primarily composed of quartz and orthoclase, whereas the MMG sample contains quartz together with feldspars and clay minerals. Despite this complexity, quartz reflections remain the most distinctive features in both datasets, with the (100), (101) and (112) reflections clearly identifiable at approximately 2.3° , 2.95° and 5.4° 2θ , respectively (consistent with α -quartz diffraction patterns reported by Le Page and Donnay, 1976). These characteristic peaks provide robust markers for phase identification even in the presence of additional silicate phases.

Overall, the analysed sample suite demonstrates that high-quality diffraction data can be obtained from a wide range of geological materials spanning varied mineralogies, grain sizes and crystallographic complexities. The results further highlight that the availability of peak-free regions identified in Sections 3A and 3B is sufficient to permit reliable phase identification for many of the rock types routinely investigated using the Mjólnir platform.

D) Optimal configuration considering sample and vessel diffraction patterns

The combination of vessel materials with various samples can now easily be made using results provided in figure 2 to 5 and using theoretical predictions. However, it may be difficult to predict exactly the relative peak intensity without a more complex model, because the sample receives a filtered beam from the vessel. To address this relative intensity uncertainty and easily visualise the potential overlap between components and sample peaks, we have in this section scanned different combinations between the samples, additional inner components (jackets and baffles) and pressure vessels, to provide experiment-like patterns. These results are summarized in figure 6.

Clear and well-resolved diffraction patterns were obtained for all tested geological samples through aluminium pressure vessels. In most cases, sample peaks were well separated from those arising from the vessel walls, confirming that aluminium vessels do not significantly interfere with the principal reflections of common silicate, carbonate and sulfate minerals (at the chosen beam energy of 72 keV). This was particularly evident for sulfate phases such as gypsum, whose low- 2θ reflections lie in regions largely free of aluminium peaks. Calcite had a similar match with aluminium vessels with first characteristic peaks in the same region and additional peaks in between (201) and (311) peaks of the vessel (between 5° and 7°). The results were broadly similar for quartz and the silicate samples, with characteristic peaks occurring both below and above the main and most intense aluminium peaks ((111) and (200)).

For PEEK vessels, the vessel effect is mostly located on the low part of the 2θ range. Despite peaks from PEEK being way less intense than metal vessels, the diffuse background has a clear effect on the final pattern. This still allows observing high intensity peaks from quartz such as (100) and (101) however, it may make quantitative operation more difficult with uncertainty in the baseline intensity. At high 2θ , the PEEK vessel leaves very little signal, making it suitable for all compounds with targeted peaks above 4° .

For the titanium vessel, with a PEEK baffle in the example provided in figure 6, we can see that the HCP symmetry generates significantly more peaks in the central region 4 - 8° ,

which may leave only a limited number of interference-free reflections of the sample phase. Titanium therefore appears to be the least favourable option for geological materials such as quartz or calcite.

General conclusions can be drawn from these successive tests: 1) Simple crystal structures generally produce fewer diffraction reflections within a given angular range and therefore tend to leave larger regions of reciprocal space accessible for sample diffraction. Low atomic number alloys are better to limit attenuation, but the material nature and vessel size (influencing the peak doublet spacing) can be tuned to favour a specific sample. 2) Avoid sample nature close to the vessel nature in crystallography and composition as peaks may overlap. Metal vessels are suited for ceramics, plastics and rock materials (except minerals that are mostly metal-like, with crystal structures and bonding resembling those found in metallic alloys), while plastic and ceramic vessels are suitable for metals. This comes with a limitation on the maximum attainable pressure and temperature conditions, which are different from tomography where more robust materials only affect the transmission and image contrast and frequency. 3) The more complex the rig, inner components and the sample, the more difficult it is to find free 2Θ space to identify and proceed to quantitative analyses of the desired peaks. In this regard, Heitt Mjölur, in its high temperature mode (combining metal vessel, PEEK baffles, copper jacket and graphite sleeves) is a more challenging rig to deploy and use at diffraction beamlines. This requires careful planning and design work depending on the sample nature and the components signature given in this manuscript.

3.2 Controls on diffraction signal quality in transmission through miniature triaxial rigs

The previous section identifies the diffraction signatures of the principal pressure vessels, internal components and geological samples. These observations provide a practical basis for selecting compatible sample–rig combinations. However, successful diffraction experiments through miniature triaxial rigs also require consideration of the physical parameters that control signal quality. In transmission geometry, the measured diffraction pattern is affected by attenuation through the pressure vessel and sample, the illuminated sample volume, grain statistics, detector geometry and acquisition strategy. This section summarises these controls and provides simple design relationships to support experimental planning and optimisation of the beamline configuration.

A) Transmission and attenuation from rig components

All materials intercepted by the incident or diffracted beam affect the measured diffraction pattern. In miniature triaxial rigs, this includes the pressure vessel, sample jacket, baffles, confining medium, pistons and, depending on the beam position, other internal components. These materials influence the experiment in two distinct ways. First, they attenuate the beam and reduce the photon flux reaching the sample or detector. Second, crystalline or semicrystalline materials generate their own diffraction signal, which may overlap with diffraction peaks from the specimen.

Beam attenuation follows Beer–Lambert law:

$$I = I_0 e^{-\mu t} \quad (3)$$

When several materials are crossed, this becomes:

$$I = I_0 e^{-\sum_i \mu_i t_i} \quad (4)$$

where I_0 is the incident intensity, I is the transmitted intensity after passing through the material, μ is the linear attenuation coefficient (of a material i), and t is the path length through

the attenuating material. The attenuation coefficient depends on composition, density and X-ray energy/wavelength. This means that pressure-vessel transmission is not controlled by wall thickness alone, but by the combination of material, density, beam energy and crossed thickness.

For a diffraction experiment through a pressure vessel, attenuation affects both the incident and diffracted beams. Conceptually, the measured intensity of a given sample reflection ($I_{hkl,obs}$) can be written as:

$$I_{hkl,obs} \propto I_0 T_{in} S_{hkl} V_{diff} T_{out} \eta_{det} t_{exp} \quad (5)$$

where T_{in} is the transmission of the incident beam before it reaches the diffracting volume, T_{out} is the transmission of the diffracted beam between the diffracting volume and detector, S_{hkl} represents the crystallographic scattering contribution of the reflection, V_{diff} is the illuminated diffracting volume, η_{det} is the detector efficiency and t_{exp} is the exposure time (Cullity & Stock, 2014). The crystallographic term S_{hkl} includes the phase fraction, structure factor, multiplicity, preferred orientation and other reflection-specific effects. Therefore, peak height or maximum counts per second cannot be interpreted directly as a measure of transmission (as opposed to intensity in transmission imaging).

This distinction is important for interpreting the vessel patterns reported above (figures 3-6). Metallic pressure vessels produced more intense, sharp and well-defined diffraction peaks than rock materials and semicrystalline components, but this does not mean that their attenuation on the beam is not important. The absolute XRD pattern count value (see max intensity metrics in figures 3-6) thus reflects the crystallinity, electron density, structure factors of each part that form continuous diffracting volumes in the beam path. For this reason, the maximum counts per second reported should be treated as an empirical measure of detector loading and practical signal strength, rather than as a direct proxy for attenuation. A more direct estimate of transmission would require either direct-beam/photodiode measurements before and after each component, or calculation from tabulated attenuation coefficients at the relevant energy and path length (see Freitas et al. 2024). Although attenuation remains an important experimental consideration, diffracted intensity cannot be interpreted in the same direct manner as transmitted intensity in radiography or tomography because it additionally depends on the crystallographic properties and illuminated volume of each contributing material.

B) Diffracting volume, sample thickness and absorption geometry

In transmission diffraction experiments, the illuminated sample volume is controlled by both the incident beam dimensions and the path length traversed through the specimen. Unlike conventional powder diffraction geometries, where sample thickness is often minimised, miniature triaxial rigs are specifically designed to investigate representative sample volumes under realistic boundary conditions. Consequently, the diffracting volume and associated X-ray path length become important parameters governing diffraction signal quality.

For a cylindrical specimen of radius R , the path length intersected by the beam varies as a function of beam position across the sample diameter. If the beam is positioned at an offset δ from the sample centre, the traversed thickness corresponds to the chord length $L(\delta)$:

$$L(\delta) = 2\sqrt{R^2 - \delta^2} \quad (7)$$

The illuminated diffracting volume may then be approximated as (considering small beam size compared to sample size):

$$V_{(diff)(\delta)} = A_{(beam)} L(\delta) \quad (8)$$

where A_{beam} is the beam cross-sectional area. For the I15 configuration used in this study (120×80 μm), the illuminated volume therefore scales directly with the path length through the specimen. The largest diffracting volume is obtained at the sample centre, where the beam traverses the entire sample diameter, while progressively smaller volumes are sampled towards the specimen edge (see figure S2).

In the absence of significant absorption, the integrated diffracted intensity is expected to scale approximately with the illuminated volume. However, increasing path length simultaneously increases both the number of diffracting crystallites and the attenuation experienced by the incident and diffracted beams. A simplified representation of the competition between increasing diffracting volume and beam attenuation is:

$$I_{(hkl)(\delta)} \propto S_{(hkl)} L(\delta) \exp[-\mu_{\text{eff}} L(\delta)] \quad (9)$$

where S_{hkl} describes the scattering contribution of the reflection and μ_{eff} represents an effective attenuation coefficient accounting for absorption of both the incident and diffracted beams. In weakly absorbing systems, intensity is therefore expected to follow the sample geometry. In more strongly absorbing materials, the increase in diffracting volume is progressively offset by attenuation effects. Consequently, intensity variations observed during diffraction mapping should not automatically be interpreted as phase abundance variations, reaction progress or preferred orientation, since part of the signal variation may originate from geometric effects alone.

The finite thickness of the illuminated volume can also influence diffraction peak shape. Because diffraction originates from a volume extending along the beam direction, different parts of the sample are located at slightly different distances from the detector. A first-order estimate of the associated geometric broadening is:

$$\Delta(2\theta)_{\text{geom}} \approx \frac{L}{D} \tan(2\theta) \quad (10)$$

where L is the path length through the specimen and D is the sample–detector distance (Copley et al. 2022). For the detector distances and comparatively small diffraction angles used in the present high-energy geometry, the broadening predicted by this relationship remains modest (<0.07° for a 3.2 mm sample, at 72 keV and $D=885.7$ mm). Geometric broadening is therefore present but not a dominant contribution to peak width in the present configuration (detector resolution of about 0.011°).

A more significant consequence of increasing path length is the averaging of diffraction information over larger material volumes. In heterogeneous samples, a single measurement may integrate multiple phases, grain populations, stress states or microstructural domains, contributing to peak broadening, asymmetry and intensity redistribution. The total peak width may therefore be expressed as:

$$\beta_{\text{total}} = \sqrt{\beta_{\text{inst}}^2 + \beta_{\text{geom}}^2 + \beta_{\text{sample}}^2} \quad (11)$$

where β_{inst} is the instrument broadening, β_{geom} the geometry broadening and β_{sample} encompasses broadening associated with grain statistics, strain heterogeneity, phase heterogeneity and crystallographic texture (Cullity & Stock, 2014; Young, 1993).

These considerations highlight a fundamental trade-off when working with representative sample volumes. Larger path lengths improve statistical representativity and increase the diffracted signal, but also increase attenuation and the averaging of spatially heterogeneous crystallographic states. Consequently, experiments aimed at bulk phase evolution, reaction progress or representative stress measurements often benefit from larger sampled volumes, whereas studies requiring maximum angular resolution or high-precision structural refinement may favour smaller path lengths and more homogeneous specimens.

C) Grain statistics and rotational averaging

The quality of diffraction data obtained from geological materials is strongly controlled by grain statistics. In an ideal powder specimen, a sufficiently large number of randomly oriented crystallites simultaneously satisfy the Bragg condition, producing continuous Debye–Scherrer rings and stable peak intensities. In contrast, coarse-grained geological materials often contain relatively few crystallites within the illuminated volume that satisfy the diffraction condition at a given orientation, resulting in spotty diffraction patterns and large intensity fluctuations between reflections. This effect becomes particularly important when investigating representative sample volumes rather than finely ground powders.

A first-order estimate of the number of grains sampled by the beam can be expressed as:

$$N \approx \frac{V_{diff}}{d_g^3} \quad (12)$$

where V_{diff} is the illuminated diffracting volume and d_g is a characteristic grain size. Although geological materials typically exhibit broad grain-size distributions and complex polymineralic fabrics, this relationship illustrates the principal control exerted by grain size. For a fixed beam size, smaller grain sizes improve powder statistics by increasing the number of crystallites contributing to diffraction, whereas coarse-grained rocks may contain too few diffracting grains to produce continuous diffraction rings and stable peak intensities.

This behaviour was observed throughout the present study (Figure S4 and S5). Fine-grained materials such as chalk and clay-rich mudstones produced nearly continuous diffraction rings even during static acquisitions. By contrast, coarser-grained materials, including quartz-rich sandstones, marble and gypsum-bearing rocks (grain sizes ranging from tens of microns to sub-millimetre), generated spotty diffraction patterns under identical acquisition conditions. In these cases, diffraction peaks could be dominated by a limited number of grains whose orientations happened to fulfil the Bragg condition during the acquisition.

One of the principal advantages of the Mjölñir suite is that the rotational symmetry can also be exploited to improve diffraction statistics. The specimen can be rotated over an angular interval $\Delta\omega$, allowing additional crystallites to fulfil the diffraction condition. The measured diffraction pattern therefore becomes an angular average of multiple sample orientations:

$$I_{hkl}^{rock} = \frac{1}{\Delta\omega} \int_{\omega_1}^{\omega_2} I_{hkl}(\omega) d\omega \quad (13)$$

where $I_{hkl}(\omega)$ is the intensity measured at a rotation angle ω . Increasing the rocking interval increases the sampled orientation space and reduces the influence of individual strongly diffracting grains. Diffraction rings therefore become progressively more continuous and approach ideal powder diffraction behaviour. The benefits of rotational averaging become increasingly important as grain size increases and powder statistics deteriorate. Practical implementation through rocking and sweeping acquisitions is discussed in Section 4.

Rotational averaging represents a major advantage of tomography-oriented deformation rigs because it improves powder statistics while preserving representative sample geometries, boundary conditions and stress states. Consequently, natural coarse-grained materials can be investigated directly, rather than relying on synthetic fine-grained analogues designed primarily to improve diffraction quality.

D) Detector distance and angular resolution

Detector distance is a key parameter controlling diffraction quality in miniature triaxial rigs because it governs angular resolution, peak separation and reciprocal-space coverage. Because most geological materials investigated at high-energy synchrotron beamlines exhibit their strongest and most diagnostic reflections at low scattering angles, optimisation of detector distance is often a critical step in experimental design.

The geometry of a two-dimensional detector is described by:

$$r = D \tan(2\theta) \quad (14)$$

where r is the radial distance of a diffraction ring from the direct beam position and D is the sample–detector distance. At the relatively small diffraction angles encountered at 72 keV, the small-angle approximation:

$$r \approx D(2\theta) \quad (15)$$

is generally valid. Consequently, the separation between neighbouring reflections scales directly with detector distance:

$$\Delta r \approx D \Delta(2\theta) \quad (16)$$

Increasing detector distance spreads diffraction rings over a larger detector area, improving both peak separation and angular sampling. For the Pilatus3X CdTe detector used in this study (172 μm pixel size), the angular interval represented by a single pixel is approximately:

$$\Delta(2\theta)_{\text{pix}} \approx \frac{p}{D} \quad (17)$$

Increasing the detector distance from 469 mm to 886 mm improves angular sampling by nearly a factor of two, enabling more effective resolution of closely spaced low-angle reflections. This is particularly important for miniature triaxial rigs, where pressure vessels produce characteristic diffraction doublets from the upstream and downstream vessel walls. Increasing detector distance improves the separation and sampling of these reflections, making them easier to resolve and model (Figures 3 and 6).

The principal disadvantage of increasing detector distance is a reduction in the accessible angular range. For a detector of fixed dimensions, the maximum observable diffraction angle is given by:

$$2\theta_{\text{max}} = \tan^{-1} \left(\frac{r_{\text{max}}}{D} \right) \quad (18)$$

where r_{max} is the maximum usable detector radius. Larger detector distances improve angular resolution at the expense of reciprocal-space coverage. For the short wavelength used in this study (72 keV; $\lambda = 0.1722 \text{ \AA}$), this trade-off is relatively favourable because most reflections from common silicates, carbonates and sulfates remain accessible even at large detector distances. The scattering-vector magnitude is given by:

$$Q = \frac{4\pi}{\lambda} \sin \theta \quad (19)$$

and the choice of detector distance therefore ultimately determines the balance between reciprocal-space coverage and angular resolution. Detector distances approaching 900 mm appear particularly favourable for phase identification, stress analysis and quantitative peak fitting in the Mjöltnir geometry, whereas shorter distances may be preferred when maximising reciprocal-space coverage is the primary objective. Because Bragg peak positions are independent of detector distance when expressed in 2θ or d -spacing, the detector position can be optimised for each experiment provided that the geometry is recalibrated following any configuration change.

E) Practical implications for experiment design

Diffraction quality in miniature triaxial rigs is controlled by vessel diffraction, beam attenuation, sample geometry, grain statistics and detector configuration. Successful

experiments therefore require coordinated selection of the pressure vessel, ancillary components, acquisition strategy and detector geometry according to the scientific objective.

A practical workflow is to first define the pressure-temperature conditions and sample characteristics, then select an appropriate vessel material. Preliminary diffraction measurements or numerical predictions can subsequently be used to assess potential overlap between vessel and sample reflections. Acquisition mode should then be chosen according to grain size and required temporal resolution, while detector distance can be adjusted to balance angular resolution against reciprocal-space coverage.

The results presented here demonstrate that representative geological sample volumes can yield diffraction data suitable for phase identification, reaction tracking and strain analysis, provided that the experimental geometry is appropriately optimised. The principal challenge is therefore not diffraction through the pressure vessel itself, but the selection of an experimental configuration appropriate to the sample, beamline and intended analysis. The modular design of the Mjölñir suite provides additional flexibility for adapting future configurations to specific high-energy XRD applications.

4. Acquisition strategies and beamline operation

The final methodological consideration, in addition to rig configuration, vessel selection and detector setup, is the choice of acquisition strategy. While the diffraction quality attainable through miniature triaxial rigs is controlled by the physical constraints discussed in Section 3, the type of information ultimately recovered depends on how the sample is illuminated and moved during acquisition. The rotational symmetry originally developed for synchrotron microtomography provides a unique degree of flexibility, enabling a range of diffraction modes spanning localised measurements, bulk phase analysis and spatially resolved mapping.

The choice of acquisition mode is primarily governed by the balance required between temporal resolution, spatial resolution, powder statistics and sample heterogeneity. Depending on the scientific objective, diffraction measurements can therefore be acquired from a single point within the sample, averaged over a rotational interval, collected continuously during rotation, or combined with translational motion to generate one- or two-dimensional maps. Figure S4 summarises the geometry and sampled volume associated with each acquisition strategy discussed below.

A) Single-point acquisition

The simplest acquisition mode consists of illuminating a fixed point within the specimen while maintaining both sample position and orientation constant. In this geometry, the sampled volume is defined by the beam cross-section and the path length through the specimen, as described in Section 3. For a centred beam, the illuminated volume corresponds to the full sample diameter intersected by the incident beam (here $120 \times 80 \mu\text{m}^2$), whereas off-centre measurements probe progressively smaller sample volumes.

Single-point acquisitions provide the highest temporal resolution and require no sample motion during exposure. In the present experiments, diffraction patterns of sufficient quality for phase identification were routinely obtained within 1 s for both Mjölñir and Heitt Mjölñir configurations, although shorter acquisitions were possible at the expense of signal quality. This mode is therefore particularly suitable for time-resolved experiments where diffraction data must be collected rapidly and repeatedly throughout the evolution of a process.

The principal limitation is the sensitivity to grain statistics due to the limited probed volume (see figure S3). Fine-grained materials generally produce high-quality powder-like patterns, whereas coarse-grained rocks may yield highly spotty diffraction with strong intensity

variations between successive measurements (see figures S3 and S4). Consequently, single-point acquisition is most effective for homogeneous materials, fine-grained samples or experiments where temporal resolution is prioritised over powder averaging.

B) Rocking acquisition

Rocking acquisitions exploit the continuous sample rotation (up to 360°) enabled by the Mjöltnir suite. During acquisition, the specimen is rotated through a defined angular interval while acquiring the diffraction image. The resulting pattern is then integrated into a single dataset. For example, a 5 s, 20° rocking acquisition rotates the specimen through 20° during a 5 s exposure. The resulting diffraction pattern therefore represents an angular average of multiple sample orientations.

Such acquisition improves powder statistics through rotational averaging and is particularly beneficial for coarse-grained geological materials (Section 3.2C). In the present study, rotational ranges of only a few degrees were sufficient to transform highly spotty diffraction patterns into continuous diffraction rings suitable for phase identification and peak fitting (Figures S3 and S4). Larger rocking ranges further improve ring continuity but progressively average orientation-dependent information.

Finally, rocking acquisition provides an effective compromise between diffraction quality and experimental simplicity. Its principal limitation is that angular heterogeneity is averaged during acquisition, and the specimen must subsequently be rotated back to its initial position before the next measurement.

C) Sweeping acquisition

Rocking acquisition maximises powder averaging but integrates the entire angular interval into a single diffraction pattern. To retain information related to crystallographic orientation and sample heterogeneity, a hybrid acquisition strategy was developed in which the specimen rotates continuously while diffraction images are acquired over successive narrow angular intervals. This approach is referred to here as sweeping acquisition.

In sweeping mode, the stage performs a continuous “fly-scan” while diffraction images are recorded at fixed angular increments. Each individual frame therefore samples a limited angular range while the complete dataset captures the evolution of diffraction intensity as a function of sample rotation. Compared with conventional stepwise rotation, this approach significantly reduces acquisition time by eliminating repeated acceleration and deceleration of the rotation stage.

Sweeping acquisitions occupy an intermediate position between static and rocking modes. Individual frames retain information on crystallographic orientation and sample heterogeneity, while the complete dataset benefits from rotational averaging across the sweep interval.

The principal limitation of sweeping acquisition is data volume. Detector readout speed limits the number of images that can be acquired continuously during a fly-scan. For the Pilatus CdTe 2M detector at I15, acquisitions spaced at 0.2° over a 90° rotation (total scan time of 2 minutes per sweep) approached the practical detector output limit. Rocking is generally preferable for phase identification and quantitative analysis, whereas sweeping additionally preserves information related to orientation and microstructural heterogeneity.

D) Vertical profiling and two-dimensional mapping

The simplest implementation consists of vertical profiling, in which diffraction patterns are acquired at multiple heights along the sample axis. This approach is particularly useful for

identifying stratification, reaction fronts or localised deformation zones while maintaining relatively short acquisition times. When centred on the sample axis, vertical profiles probe comparable sample volumes at each position and facilitate direct comparison between measurements.

By extending this strategy to both horizontal and vertical directions, two-dimensional diffraction maps can be generated. Rotational acquisition modes (rocking or sweeping) are generally not suitable during mapping because off-centre measurements would introduce variable path lengths through the sample, pressure vessel and ancillary components. Consequently, spatial variations in diffraction geometry would become difficult to distinguish from genuine sample heterogeneity. However, depending on acquisition conditions, these maps may reveal spatial variations in phase abundance, crystallographic texture or stress state.

Mapping experiments are inherently slower than stationary acquisitions because each position requires stage motion. For example, a map comprising 400 individual acquisitions was acquired in 45 min at I15. Away from the sample centre, both the crossed sample thickness and vessel path length vary (Section 3; Figure S3), introducing changes in peak shape and intensity that are unrelated to material variability. These geometric effects must therefore be considered during interpretation of diffraction maps.

E) Toward diffraction computed tomography

The combination of high-energy transmission geometry, rotational symmetry and spatial scanning naturally provides a pathway toward diffraction-imaging approaches such as scanning 3DXRD and diffraction-computed tomography. Although these methodologies fall beyond the scope of the present study, the acquisition strategies described here constitute many of the experimental building blocks required for their implementation within miniature triaxial rigs.

Recent studies have demonstrated the potential of coupling diffraction-based measurements with deformation experiments to resolve grain-scale stress evolution, crystallographic orientation and microstructural heterogeneity within geological materials (Jacob et al., 2025; Hurley et al., 2025). These approaches rely on precise sample positioning, rotational acquisition and careful optimisation of detector geometry, all of which are directly compatible with the experimental framework presented here.

The primary objective of this work is therefore not to develop diffraction tomography itself, but to establish practical methodologies for acquiring high-quality diffraction data through tomography-oriented deformation apparatus. In this context, diffraction tomography should be viewed as a natural extension of the experimental framework presented here rather than its primary objective.

5. Example of applications

This final section illustrates representative application domains enabled by the combination of miniature triaxial microtomography rigs and time-resolved X-ray diffraction. Rather than presenting complete scientific case studies, which will be reported elsewhere, the objective here is to demonstrate the types of data acquisition strategies and scientific questions that become accessible with this newly established capability.

The examples below build directly on the methodological developments described in Sections 2, 3 and 4 and are intended to highlight feasibility, complementarity with microtomography, and potential impact across a range of materials sciences and geosciences studies.

A) Qualitative and quantitative tracking of phase transformations (phase identification) and reaction progress (phase proportion)

Time-resolved XRD enables phase transformations to be monitored under pressure, temperature and stress conditions representative of the subsurface. A particular advantage of diffraction is its sensitivity to the earliest stages of a reaction, when newly formed phases may generate measurable diffraction peaks long before they become resolvable in reconstructed tomographic volumes.

In many geological and engineering systems, reaction products initially nucleate as crystallites or fine-scale intergrowths far below the spatial resolution of microtomographic imaging. These newly formed phases may nevertheless generate measurable diffraction peaks, allowing their detection long before they become visible in reconstructed tomographic volumes (Shrank et al. 2020, Chen et al. 2021). Diffraction can therefore provide an early-warning indicator of reaction initiation, while tomography subsequently characterises the associated evolution of porosity, damage, fluid pathways and reaction textures. The combination of both techniques thus offers a continuous link between crystallographic transformations and their macroscopic microstructural consequences.

The large sample volumes accommodated by the Mjölur rig suite, together with acquisition times of only a few seconds, enable mineralogical evolution to be monitored continuously throughout an experiment. Depending on acquisition strategy and data quality, diffraction measurements can be used both qualitatively, through the appearance, disappearance or shifting of characteristic reflections, and quantitatively through analysis of peak intensities, integrated peak areas or full-pattern refinement approaches. Rocking and sweeping acquisitions additionally facilitate quantitative analysis in materials that would otherwise exhibit poor powder statistics.

A representative example is provided by tracking the dehydration of gypsum to bassanite under triaxial stress conditions. This reaction has previously been investigated using synchrotron microtomography with the Mjölur platform (Marti et al., 2021, Gilgannon et al., 2023, Rizzo et al. 2024), which enabled direct quantification of the evolution of reaction-induced porosity and fluid pathways. However, the initial formation of bassanite occurs at grain and lattice scales significantly smaller than the resolution of imaging experiments and is therefore not seen by microtomography and more readily detected using diffraction techniques. In the present study, diffraction data were collected during dehydration experiments performed at 125 °C, 20 MPa confining pressure, positive differential stress and 5 MPa pore-fluid pressure, reproducing conditions previously employed in synchrotron microtomography investigations (Gilgannon, Freitas et al. 2026). Successive diffraction datasets were acquired using a sweeping acquisition over 90°, and characteristic reflections of both gypsum and bassanite were subsequently tracked through time using Continuous Peak Fit (CPF) analysis (see supplementary method S1).

The results demonstrate the progressive disappearance of gypsum reflections accompanied by the simultaneous emergence and growth of bassanite peaks (Figure S6). Furthermore, by fitting selected non-overlapping reflections, the evolution of relative phase proportions can be estimated from changes in peak intensity and area. While monitoring phase transition with XRD is a common procedure, this dataset provides an unambiguous qualitative and quantitative record of the phase transformation through miniature triaxial cells and permits the reaction progress to be followed continuously throughout the experiment. The phase proportion evolution inferred from the diffraction data is similar to the evolution previously observed using synchrotron microtomography and phase volume segmentation under equivalent experimental conditions. Although simple, this approach provides a first approach

and quantification of reaction kinetics and enables identification of key reaction stages such as nucleation, acceleration and completion. This demonstrates the strong complementarity between the imaging and diffraction approaches and illustrates how diffraction may significantly extend the temporal sensitivity of *in situ* experiments performed with miniature triaxial rigs.

Several limitations should nevertheless be considered. First, it has to be acknowledged that at low temperatures many reactions proceed via amorphous intermediates (such as calcium carbonate system, metal sulfides, nanoparticulate phases), reactions that do not produce strong diffraction peaks. Thus, this method is only suitable for a suite of reactions producing conditions favourable for clean XRD signals. Second, when attempting quantitative phase analysis, the relative peak intensities and areas may be influenced by preferred orientation, grain statistics, changing illuminated volume, absorption and composition effects and overlap between reflections from different phases. In the gypsum–bassanite system, partial overlap between some reflections locally degrades peak-fitting quality and introduces additional data-curation steps to achieve reliable phase proportion estimates (see figure S6 and supplementary method S1).

Nevertheless, these results demonstrate that high-energy diffraction measurements performed through synchrotron microtomography deformation rigs provide data of sufficient quality to identify reaction products, crystal/lattice preferred orientation, monitor reaction progress and estimate phase evolution continuously through time. More broadly, they establish a practical route toward truly multiscale investigations in which lattice-scale phase transformations can be directly linked to evolving microstructures observed by synchrotron microtomography, thereby bridging a critical observational gap between crystallography and material-scale behaviour.

B) Structural identification and refinement in large sample volumes

A first class of applications concerns mineral identification, structural recognition and refinement in large, representative sample volumes. Conventional high-quality powder diffraction experiments at pressure, particularly those enabling Rietveld refinement (Young 1993; Cullity & Stock, 2014), typically rely on very fine-grained samples and restricted sample volumes (e.g. in diamond anvil cells). Such constraints often require extensive sample preparation and result in sample states and properties that deviate markedly from natural or engineering-relevant microstructures. This can alter key parameters such as roughness, solubility, reactive properties and kinetics, etc. because many processes critically depend on grain sizes and grain boundaries properties at mesoscale.

The rotational symmetry of microtomography rigs enables rocking and sweeping acquisitions that improve powder statistics and permit the acquisition of high-quality diffraction patterns from coarse-grained, representative sample volumes.

Fine-grained materials such as chalk (figure S4) produced quasi-ideal powder diffraction patterns with exposure times as short as 1 second and thus may not require specific angular sweep, saving acquisition time. By contrast, coarse-grained samples, including sandstones and gypsum (figure S5), initially produced spotty diffraction patterns when measured at fixed angles; however, applying rocking acquisition over a few degrees significantly reduced spottiness and improved ring continuity, enabling reliable peak fitting and phase identification.

To demonstrate the quality of data obtained, we have performed a Rietveld refinement on the final product of the gypsum dehydration experiments (measured *in situ* at completion) with the Mjölur rig (see Gilgannon et al. 2023 and Freitas et al. 2024 for methodological details). The data collected feature the peak doublet from the aluminium vessel and peaks from the main phase of the sample: bassanite (figure 8). The details of the refinement steps is given in the supplementary section S4. Our results show an excellent ability to explain the pattern with the sample and using separate aluminium phases representing the upstream and downstream vessel walls. Once the vessel signal is removed, the sample peaks are also suitable for high-quality refinement. Both peak positions and profiles were successfully reproduced as demonstrated in figure 8, with a final reduced chi-square of 0.98 and W_r of 6.288, with most of the fitting errors being linked to the complex background at low 2θ due to the silicone jacket which was not included in the phase list. At 20 MPa confining pressure, an axial load of approximately 27 MPa and 125 °C, the refined bassanite lattice parameters were $a = 12.02951\text{\AA}$, $b = 6.95528\text{\AA}$, $c = 12.70881\text{\AA}$ and $\beta = 90.198^\circ$, giving a unit-cell volume of $1063.322\text{ \AA}^3$. These refined parameters are coherent with α -bassanite and I2 space group expected for these conditions.

This capability demonstrates that quantitative phase proportion, lattice and structural information can be retrieved from materials that would otherwise be considered unsuitable for high-quality diffraction analysis, if acquisition strategies are adapted to the sample microstructure.

An inherent limitation to this approach arises from sample thickness, particularly for the larger Heitt Mjölur configuration. Increased illuminated path length can lead to peak broadening, potentially precluding full Rietveld refinement in some cases. This highlights a trade-off between representative sample volume and ultimate angular resolution that must be considered during experimental design.

As with other pressure-based diffraction techniques, this approach enables tracking of structural evolution as a function of pressure and temperature within the operational range of the selected rig. Time-resolved measurements further allow dynamic processes to be monitored, such as elastic compression or incipient phase changes, within the constraints imposed by achievable stress and temperature conditions.

C) Stress and strain quantification

In addition to phase identification, high-energy diffraction provides access to elastic strain and stress through changes in lattice spacing. Under non-hydrostatic conditions, diffraction rings become anisotropic and d-spacing varies systematically with azimuth around the Debye-Scherrer ring. These variations can be quantified through azimuthal peak fitting and related to the underlying deviatoric stress field (Singh et al., 1998; Oddershede et al., 2010). Quantifying lattice stress and strain complements the macroscopic stress/strain measurements obtained from the rig instrumentation and provides direct insight into how stresses are distributed and accommodated within individual phases.

While these variations are usually quantified by azimuthally segmenting (“caking”) the diffraction rings and fitting the position of specific reflections as a function of azimuth angle (described by a $\cos^2$ relationship with azimuth (figure S7)), CPF fittings extends this approach by directly working with the full detector panel information, without resampling, improving the quality of the data and enabling smaller lattice strains and stresses to be resolved (Hunt et al., 2019, Chen et al., 2021; Zhang et al., 2024).

The rotational symmetry of the Mjöltnir rig suite improves azimuthal coverage (reducing potential shadowing effect) and powder statistics, facilitating strain analysis in coarse-grained materials. This is particularly important for geological samples, where diffraction rings frequently exhibit strong azimuthal intensity variations and incomplete ring coverage.

To evaluate the feasibility of lattice strain and stress analysis within this experimental geometry, diffraction data collected during the dehydration experiments detailed in section 5A) were analysed using CPF (see supplementary methods S1 & S2). Peak fitting (Figures S4 and S5) demonstrated that diffraction peak positions could be determined with sufficient precision to resolve small variations in lattice spacing. The deviatoric strain can then be estimated as well as stress using Hooke's law. The results presented in figure 9 highlight a high precision of the method, with resolved strains below 0.001. The complex behaviour for each reflection points toward complex stress state reorganisation during mineral transformations.

These observations further highlight the importance of acquisition strategy. Rocking and sweeping acquisitions substantially improve ring continuity by increasing the number of crystallites contributing to the diffraction signal, thereby reducing uncertainty on peak-position determination and improving the robustness of strain analysis. Although a complete lattice strain and stress analysis is beyond the scope of the present methodological study, the results demonstrate that diffraction data collected through the Mjöltnir and Heitt Mjöltnir rigs possess sufficient quality for elastic strain measurements. This establishes the feasibility of future experiments aimed at quantifying stress evolution during deformation, monitoring stress redistribution associated with mineral reactions, and linking lattice-scale strain localisation to the development of fractures, porosity and other microstructural features observed by synchrotron microtomography. The ability to recover both crystallographic and microstructural indicators of deformation from representative sample volumes represents a significant step toward truly multiscale investigations of coupled mechanical and chemical processes.

D) Spatially resolved diffraction mapping and volumetric heterogeneity

While bulk diffraction measurements provide information averaged over the illuminated volume, many geological and engineering processes are inherently heterogeneous in space. Deformation localises into discrete zones, mineral reactions commonly propagate as reaction fronts, and fluid–rock interactions often generate strong gradients in phase abundance and microstructure. Consequently, understanding the spatial distribution of crystallographic changes can be as important as quantifying their average evolution.

The translation stages available on modern synchrotron diffraction beamlines enable diffraction measurements to be acquired at multiple positions through the sample. By combining successive point acquisitions with controlled stage motion, one- and two-dimensional diffraction maps can be generated, providing spatially resolved information on phase assemblage, reaction progress, texture and crystallographic state. Unlike conventional bulk diffraction experiments, these maps retain positional information and therefore provide insight into the internal organisation of the evolving sample.

The spatial resolution of a diffraction map is primarily controlled by the beam dimensions and step size, whereas the acquisition time depends on the number of mapped positions and exposure time per point. For the geometric configuration employed here, diffraction maps can be acquired across the full diameter or length of the specimen (figure S2), enabling comparisons between different regions of the sample while maintaining identical experimental conditions. Vertical profiling provides a rapid approach for identifying reaction

fronts or deformation localisation along the sample axis, whereas two-dimensional mapping allows lateral variations in phase distribution and crystallographic properties to be investigated.

A critical aspect of diffraction mapping in cylindrical samples is that the illuminated volume varies systematically with beam position (Section 3B) and induces corresponding variations in diffracted intensity. Consequently, intensity and peak width variations observed across a map do not necessarily reflect changes in phase abundance and must be interpreted together with the acquisition geometry. Nevertheless, systematic variations in peak position, peak shape or phase-specific reflections can provide robust evidence for genuine spatial heterogeneity within the sample.

Here, we illustrate an example of a 2D map, using the data collected prior to the gypsum dehydration reaction used in the previous sections (with an unreacted sample under confining pressure). XRD images were taken at 0.2 mm steps over a 2 x 8 mm² area centred on the sample (full details are given in supplementary section S3). Gypsum and aluminium reflections were fitted using Continuous-Peak-Fit and the combined relative peak areas are used to illustrate relative variation within the map. While in-depth interpretation of the map is beyond the scope of this study, the results show clearly larger peak areas on the side of the maps for aluminium which reflects the increase of crossed vessel thickness further away from the centre of rotation. Gypsum maps show a greater variability which may be due to relative orientation of the grain in specific areas and the presence of accessory phases such as celestite, well known in the starting material.

An important advantage of this approach is that diffraction mapping can be repeated throughout an experiment. When the characteristic timescale of the investigated process is long relative to the map acquisition time, successive maps may be collected and assembled into time-resolved diffraction datasets. This offers an integrated view across a small sample volume through time. In effect, the experiment produces a four-dimensional dataset in which crystallographic information is resolved as a function of position and time, complementing the four-dimensional microstructural information obtained from synchrotron microtomography.

The capability is particularly valuable when combined with imaging measurements. Microtomography may identify the location of features such as phases, porosity development or reaction textures, whereas diffraction mapping can determine whether these features are associated with changes in mineralogy, crystallographic texture, stress state or reaction extent. The combined methodology therefore provides a direct route for linking observed structural heterogeneity to its crystallographic origin.

These spatially resolved measurements bridge the gap between conventional bulk diffraction experiments and more advanced diffraction-tomography approaches. While full diffraction computed tomography remains significantly more demanding in terms of acquisition time, data volume and data processing (see Hurley et al. 2025 & Jacob et al. 2025 for dedicated studies), the mapping strategies described here provide a practical and experimentally accessible means of evaluating spatial heterogeneity in representative sample volumes.

F) Toward integrated crystallographic and microstructural characterisation

Combining crystallographic and microstructural measurements within a common experimental framework offers several advantages. Rather than treating diffraction and imaging as independent techniques, the approach enables observations spanning multiple scales, from lattice-scale structural changes and elastic strain to sample-scale changes in porosity, deformation and reaction textures.

The examples presented above illustrate how diffraction measurements provide access to phase evolution, structural changes, strain development and spatial heterogeneity within representative sample volumes. These observations can be directly related to the microstructural evolution previously investigated using synchrotron microtomography, creating opportunities for a more complete understanding of coupled physical and chemical processes. Both techniques provide information on stress and strain, but at different temporal and spatial scales, thereby addressing observational gaps that are inaccessible to either method alone.

Although the present study focuses on establishing the methodological framework required for diffraction experiments using the Mjölhir rig suite, the broader objective is to enable increasingly integrated investigations. Sequential diffraction and microtomography experiments can already be performed under comparable boundary conditions, while continued improvements in detector technology, acquisition speed and synchrotron brightness are progressively reducing the barriers to combined measurements.

Looking forward, this capability provides a pathway towards coordinated diffraction and microtomography studies in which crystallographic information, phase evolution, stress development and microstructural change can be investigated within the same experiment. Such approaches have the potential to bridge the long-standing gap between lattice-scale processes and bulk material behaviour across a wide range of geomaterials, energy materials and engineered systems.

Conclusions

This study demonstrates that synchrotron 4D microtomography deformation rigs can be successfully repurposed as versatile platforms for time-resolved, high-energy X-ray diffraction with sample volumes exceeding 1 cm³. Using the Mjölñir and Heitt Mjölñir rigs as examples, we show that their combination of large sample capacity, rotational symmetry and compatibility with high-energy monochromatic beams makes it possible to retrieve lattice-scale crystallographic information through pressure vessels with sufficient quality for phase identification, reaction tracking and stress analysis.

Beyond establishing feasibility, this work provides a practical and transferable methodological framework. By detailing beamline configuration, rig installation constraints, pressure-vessel material selection, theoretical reasoning and diffraction acquisition strategies, we identify the key parameters that must be considered prior to experiment design and execution. In particular, the choice of vessel material, wall thickness, beam energy, detector distance and acquisition mode are shown to critically control diffraction quality and phase resolvability. This *a priori* knowledge is essential for optimising experiments and avoiding peak interference when working with complex multiphase systems.

The results further highlight the unique advantages conferred by rotational symmetry. Rocking and sweeping acquisition strategies enable effective powder averaging in samples with grain sizes far larger than those typically compatible with conventional diffraction experiments, while preserving realistic microstructures and boundary conditions. This capability extends diffraction-based analyses to natural and engineered materials for which representative volumes and complex heterogeneity are essential, but previously inaccessible. Crucially, combining time-resolved XRD with 4D synchrotron microtomography provides a pathway toward fully coupled multiscale investigations, in which lattice-scale processes (phase transformations, elastic strain and stress) can be directly linked to evolving microstructure, porosity and damage. Such integration offers a step change relative to standalone imaging or diffraction approaches, particularly for systems where early reaction stages, subtle phase changes or stress redistribution occur below the spatial resolution of tomography.

The ease of deployment and portability of the Mjölñir rig suite further ensures that this approach can be readily adopted across diffraction beamlines, fostering methodological convergence, reproducibility and broader community uptake. Looking forward, these results pave the way for systematic dual-modality experiments combining μ CT and XRD, asynchronous or quasi-simultaneous measurements, an aspect enabled by the transition to the 4th generation of synchrotron sources and extremely bright beams.

Overall, this contribution establishes the technical foundations required to move from capability demonstration toward routine, fully integrated *in situ* experiments that quantitatively couple microstructural evolution, phase change and stress in four dimensions.

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Figures:

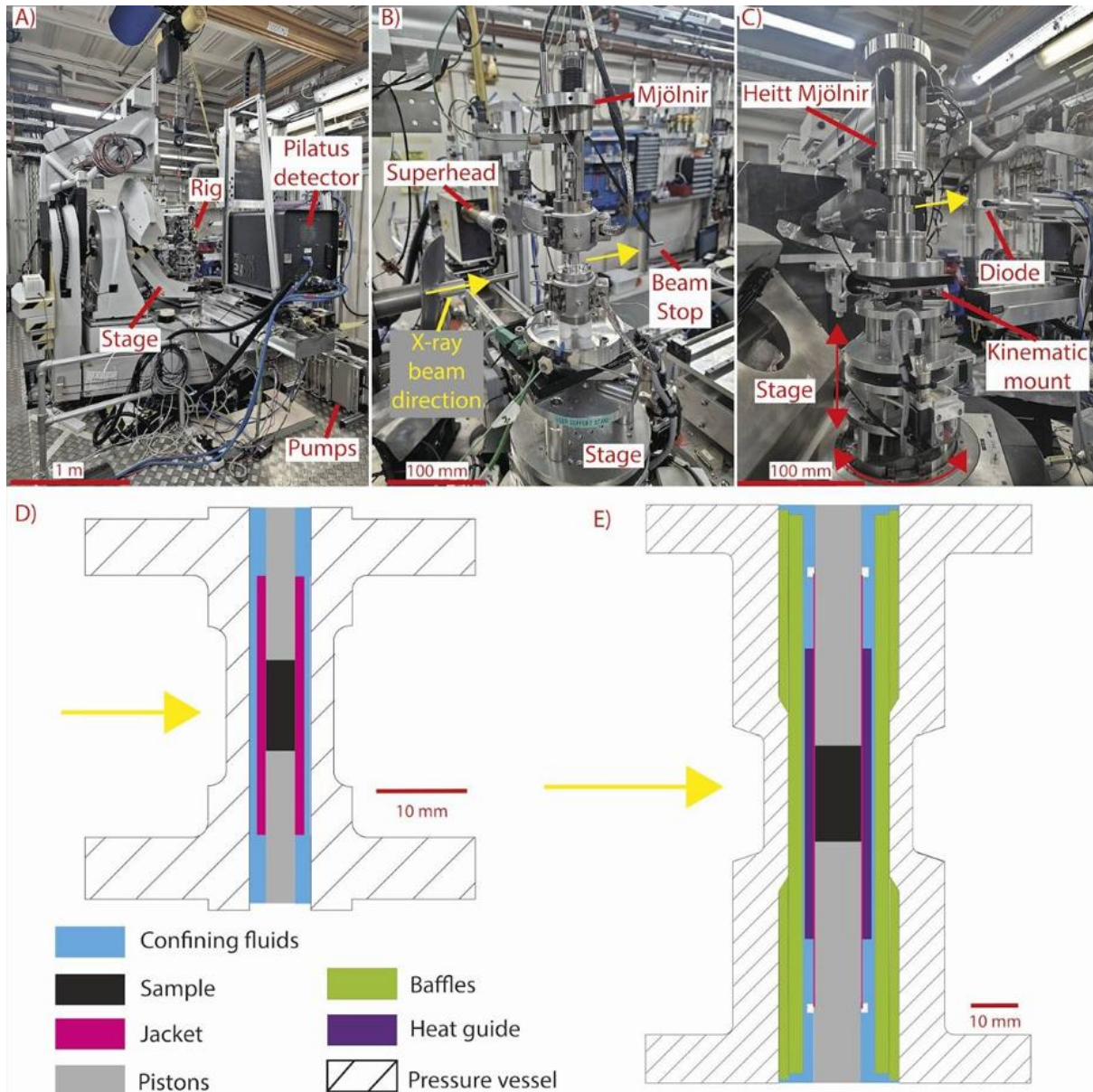


Figure 1 Photographs of the A) of the general setup at I15 beamline and B) Mjölknir and C) Heitt Mjölknir rigs installed. The Superhead and the Diode can slide on the beam path for the alignment tasks. The close proximity of the beam stop to the devices requires precise installation. D) and E) schematic cross sections of Mjölknir and Heitt Mjölknir pressure vessels showing the internal components on the beam path. Full detail of each rig's components is given in figure S1.

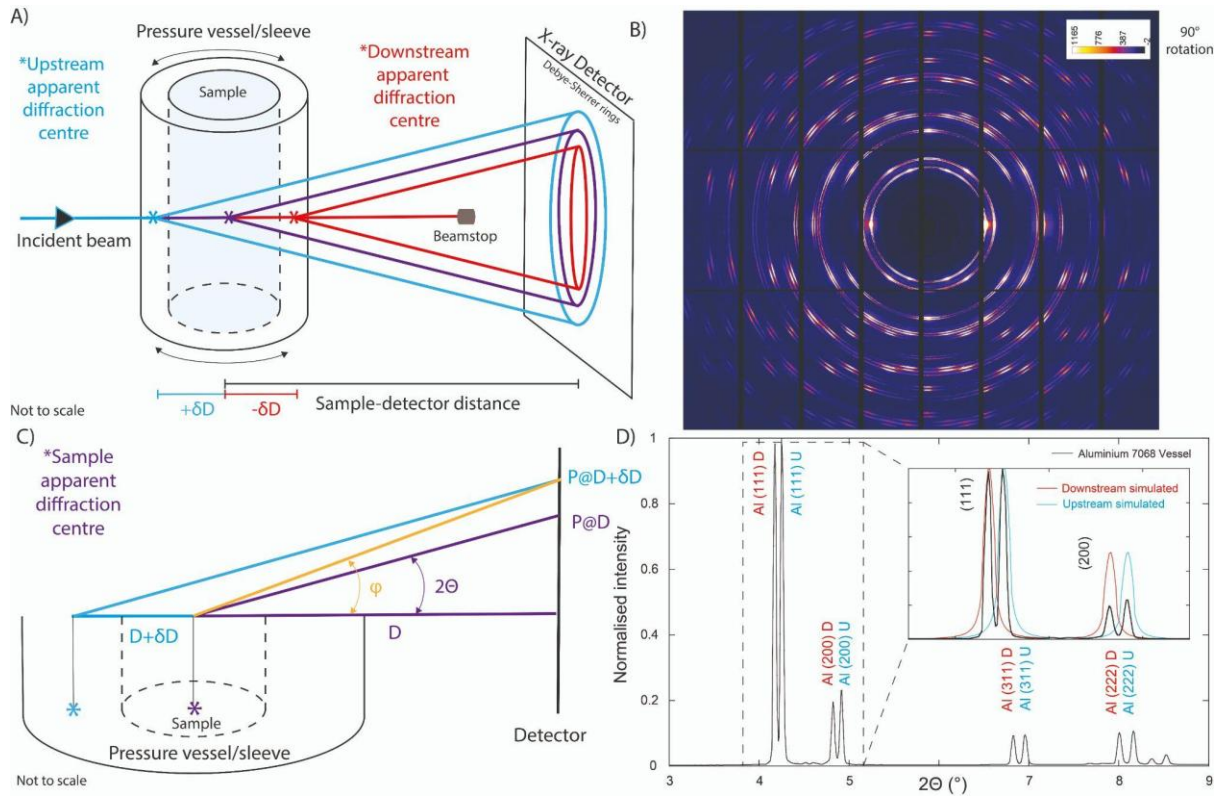


Figure 2 (A) Schematic representation of the X-ray diffraction geometry for a cylindrical sample enclosed within a tubular pressure vessel, representative of a miniature triaxial rig at a synchrotron diffraction beamline. The incident beam is shown in blue, while colours are used to distinguish diffraction from the upstream vessel wall, sample and downstream vessel wall. Each component generates a distinct diffraction pattern on the detector owing to differences in sample-to-detector distance ($\pm \delta D$). Apparent diffraction centres are indicated by asterisks (*). (B) 2D area diffractogram acquired using the Pilatus detector from an aluminium (7068) pressure vessel, showing the characteristic diffraction-peak doubling generated by the upstream and downstream vessel walls. The detector image has been rotated by 90° for display. (C) Enlarged schematic of the diffraction geometry used to calculate the apparent diffraction angle, ϕ , from the diffraction angle at the sample centre (2θ) and the offset in sample-to-detector distance (Equations 1 and 2). (D) Comparison between measured (black) and modelled diffraction patterns for the upstream (blue) and downstream (red) vessel walls. The model reproduces the observed doublet positions using Equations 1 and 2. Differences in intensity arise from beam attenuation, which is not included in the simulation.

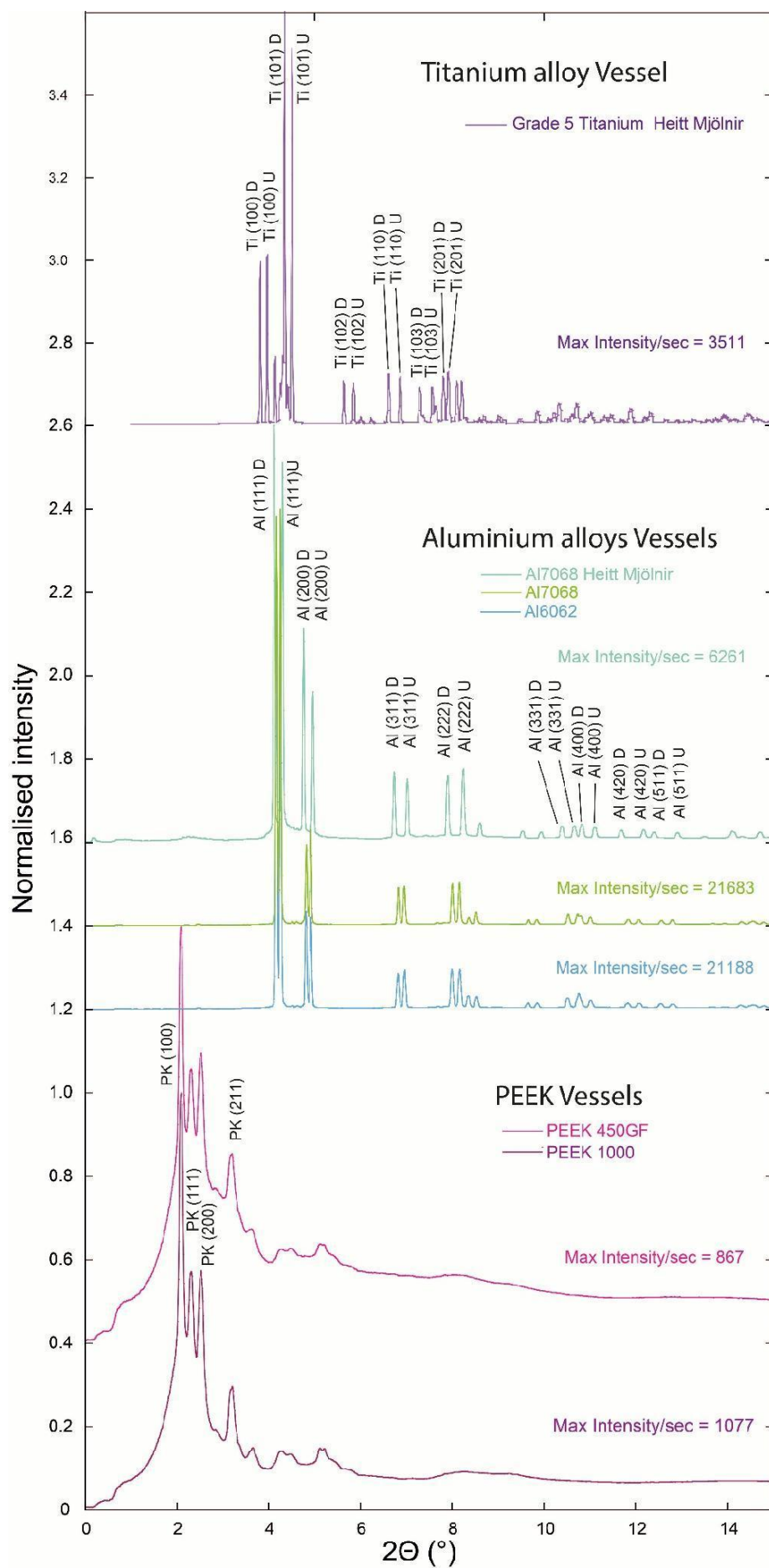


Figure 3. X-ray diffraction patterns of the pressure vessels used in the Mjöltnir and Heitt Mjöltnir rigs (where indicated), collected at 72 keV. Aluminium and titanium alloy vessels generate sharp diffraction peak doublets originating from the upstream and downstream vessel walls, leaving wide low- 2θ regions available for sample reflections. PEEK vessels exhibit the broad diffuse features typical of semicrystalline polymers and are comparatively featureless at higher diffraction angles. Intensities were normalised to the maximum value of each acquisition to facilitate comparison between datasets. The maximum counts per second (s^{-1}) of the most intense reflection are reported as an indication of absolute diffraction signal strength. All datasets were acquired at a sample-to-detector distance of 469.124 mm, except for the Heitt Mjöltnir titanium vessel (619.17 mm) and aluminium vessel (701.73 mm).

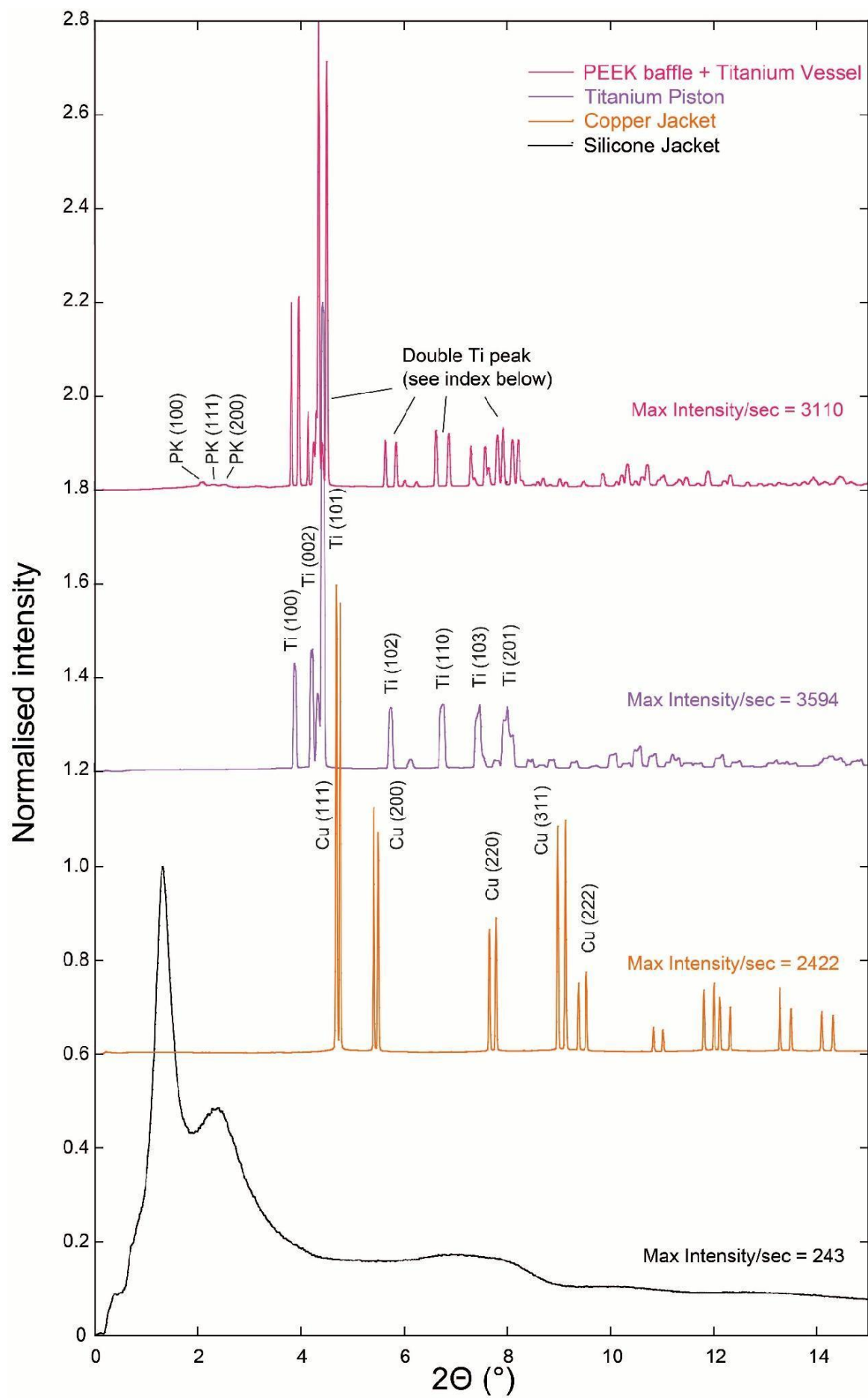


Figure 4. X-ray diffraction patterns of additional components commonly intersecting the beam path in the Mjölñir and Heitt Mjölñir rigs, including sample jackets, thermal baffles and titanium piston materials, collected at 72 keV. Intensities were normalised to the maximum value of each acquisition to enable direct comparison of diffraction patterns with different absolute signal levels. The maximum counts s^{-1} of the most intense reflection are reported as a proxy for diffraction signal strength. All datasets were acquired with a sample-to-detector distance of 469.124 mm, except for the Heitt Mjölñir titanium piston (purple), which was collected at 619.17 mm.

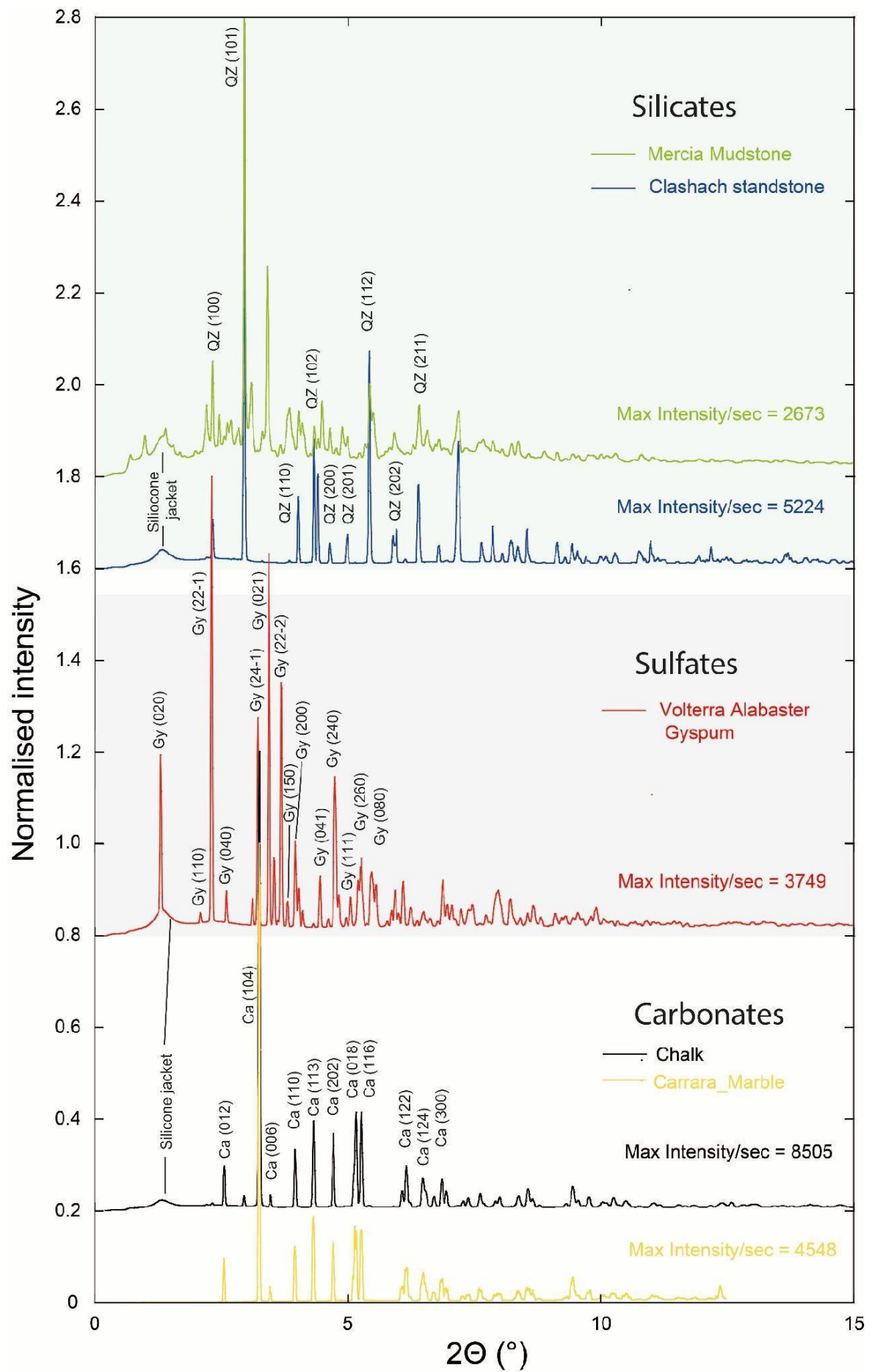


Figure 5. X-ray diffraction patterns of representative geological materials commonly investigated using the Mjöltnir and Heitt Mjöltnir rigs, including silicates, carbonates and sulfates, acquired at 72 keV. Most datasets were collected from cylindrical samples measuring 3.2 mm in diameter and 10 mm in length, except for the Carrara marble sample, which was analysed using a 10 mm diameter specimen. All 3.2 mm diameter samples were enclosed within a silicone jacket during acquisition to restrict any movement (no vessel or any other ancillary component). Principal reflections of the dominant mineral phases are indexed; additional reflections observed in the Clashach sandstone and Mercia Mudstone Group samples correspond primarily to feldspars and clay minerals. Diffraction intensities were normalised to the maximum value of each acquisition to facilitate comparison between datasets with differing absolute count rates. The maximum counts s^{-1} of the most intense reflection are reported as an indication of diffraction signal strength. All measurements were acquired with a sample-to-detector distance of 469.124 mm, except for the Carrara marble dataset, which was collected at 885.7 mm.

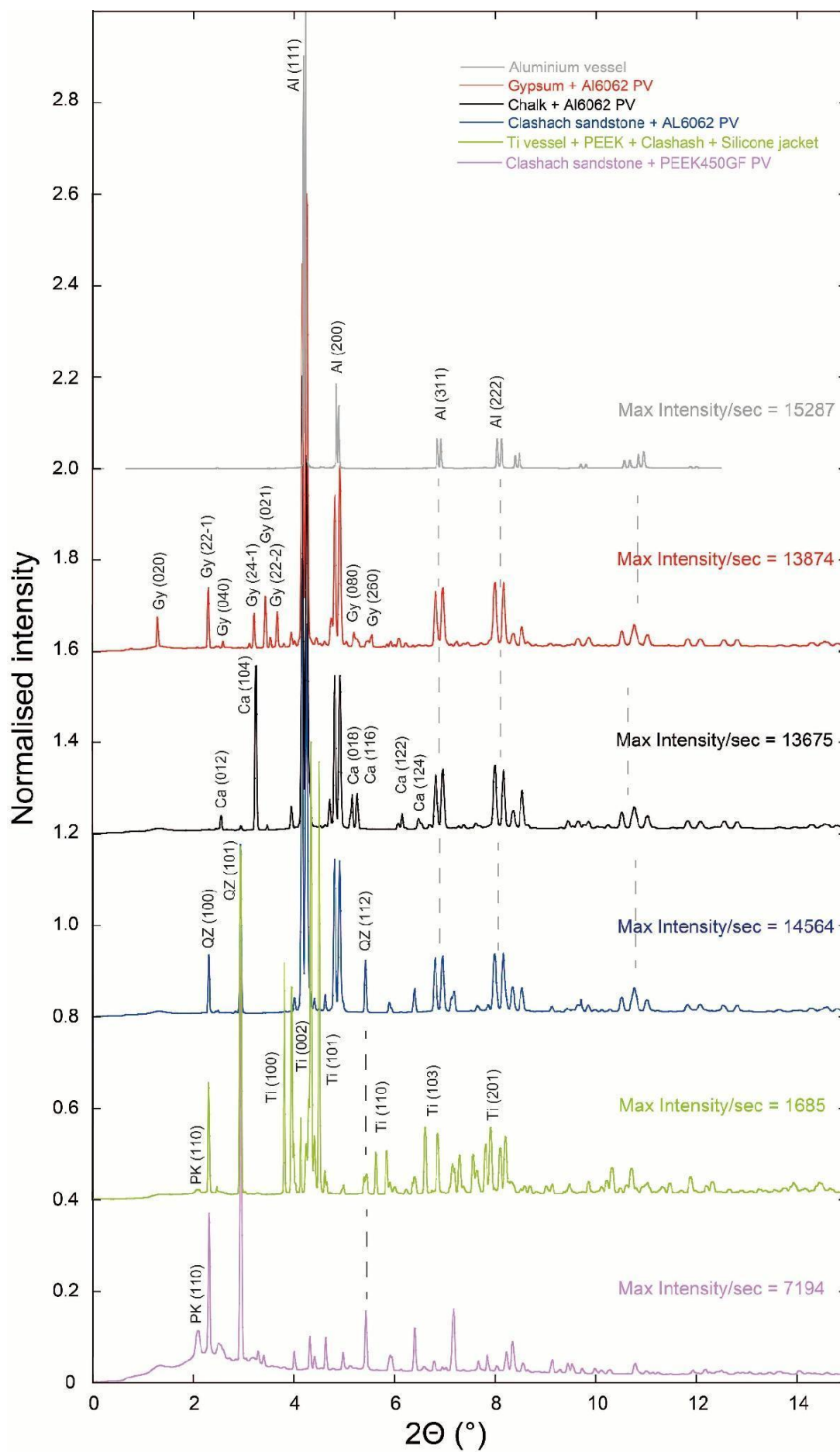


Figure 6 X-ray diffraction patterns of representative sample–rig configurations, combining geological samples with pressure vessels (PV) and, where applicable, additional rig components. These measurements provide experiment-like diffraction patterns showing the relative intensities and overlap between sample and rig-derived reflections. Metallic vessels produce intense, discrete reflections but leave substantial interference-free regions containing characteristic sulfate, carbonate and silicate peaks. PEEK vessels produce weaker diffraction peaks but contribute a broad low- 2θ background, while leaving the higher-angle region comparatively free of vessel reflections. Intensities were normalised to the maximum value of each acquisition to facilitate comparison between datasets; the maximum count rate of the most intense reflection is reported as an indication of absolute diffraction signal strength. Measurements were acquired at a sample-to-detector distance of 469.124 mm, except for the Heitt Mjöltnir configurations with the titanium vessel and PEEK baffle (619.17 mm) and the aluminium vessel (701.73 mm)

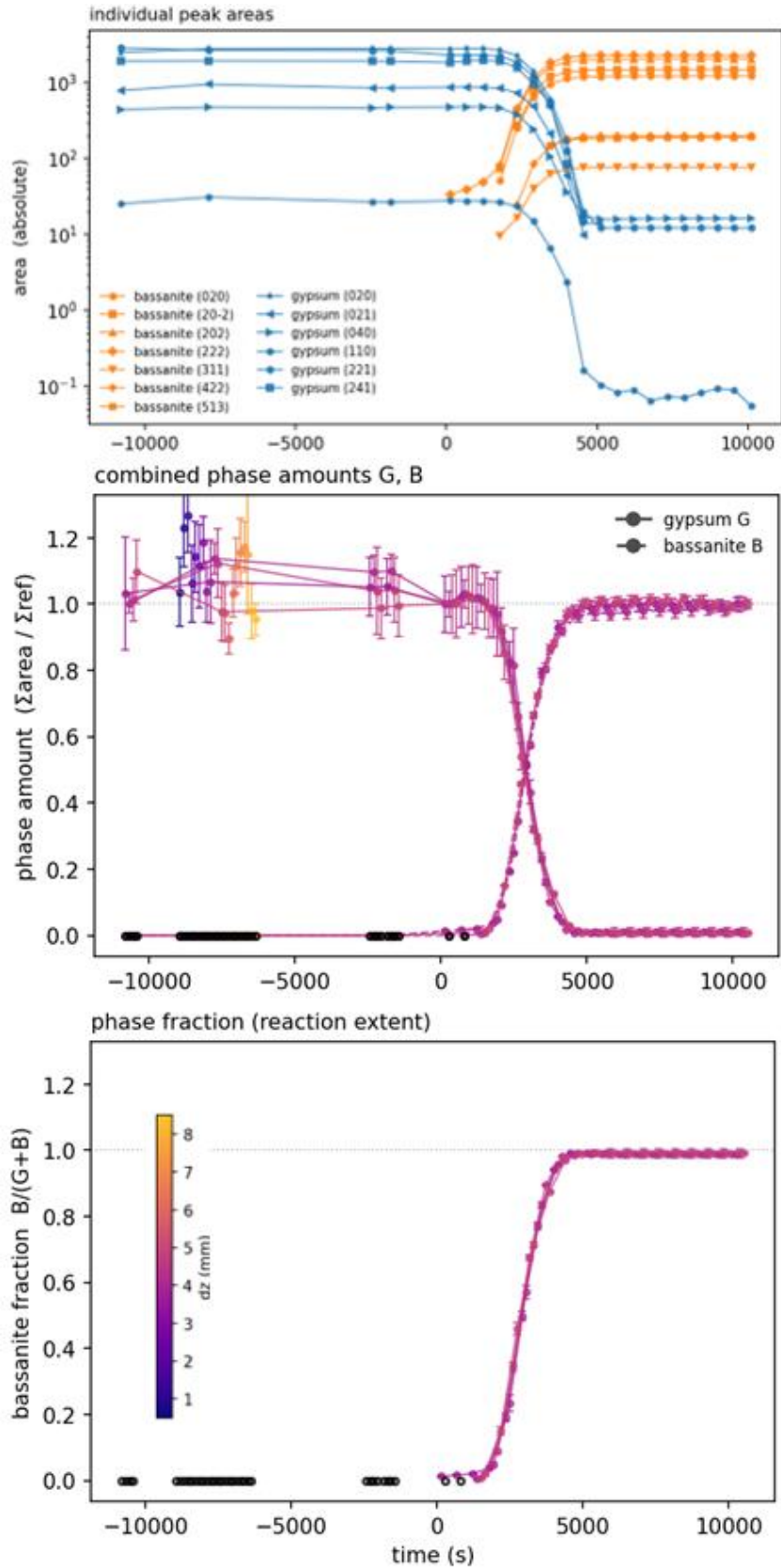


Figure 7. Phase proportion/molar fraction evolution during the gypsum-to-bassanite transformation measured during the in situ dehydration experiment. (A) Top frame, evolution of the integrated peak area of the individual gypsum (blue) and bassanite (orange) reflections tracked during the reaction. Data were acquired at a fixed position within the sample (3.7 mm from the upper interface) using a 90° sweeping acquisition. (B) Relative phase evolution calculated from the average integrated areas of the reflections shown in (A) and normalised to a

reference scan (first scan after crossing the phase boundary for gypsum; final scan prior to cooling for bassanite). (C) Conversion curves calculated from the combined gypsum (G) and bassanite (B) integrated peak areas and normalised such that the total phase fraction remains between 0 and 1. Colours represent measurements acquired at different depths within the sample. For clarity, outliers have been removed from the plot. Time has been set to 0 at the moment when the temperature exceeds 100.6°C, the estimated gypsum-bassanite phase boundary (see Gilgannon et al. 2023).

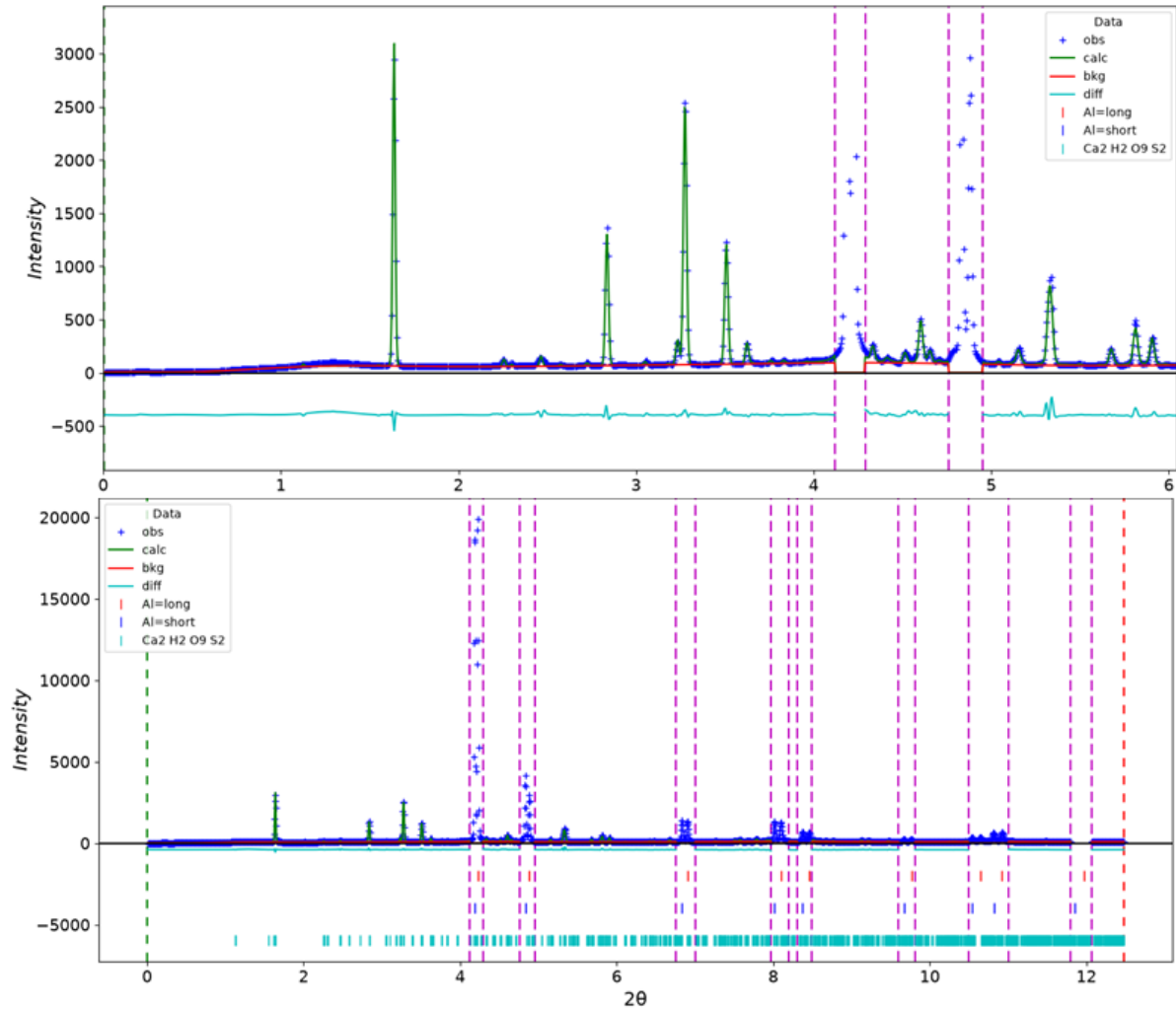


Figure 8 Rietveld refinement of the final dehydration products of the gypsum–bassanite reaction. The lower panel shows the full 2θ range, with the measured signal combining contributions from the sample, jacket, and vessel. Regions containing vessel diffraction peaks (upstream in red and downstream in blue), delimited by purple dashed lines, were excluded from the sample refinement. The upper panel shows an enlarged view of the low- 2θ region, where the main bassanite peaks are concentrated. Observed data are represented by blue crosses, the calculated fit by the green line, the background by the red line, and the difference between observed and calculated intensities by the cyan curve.

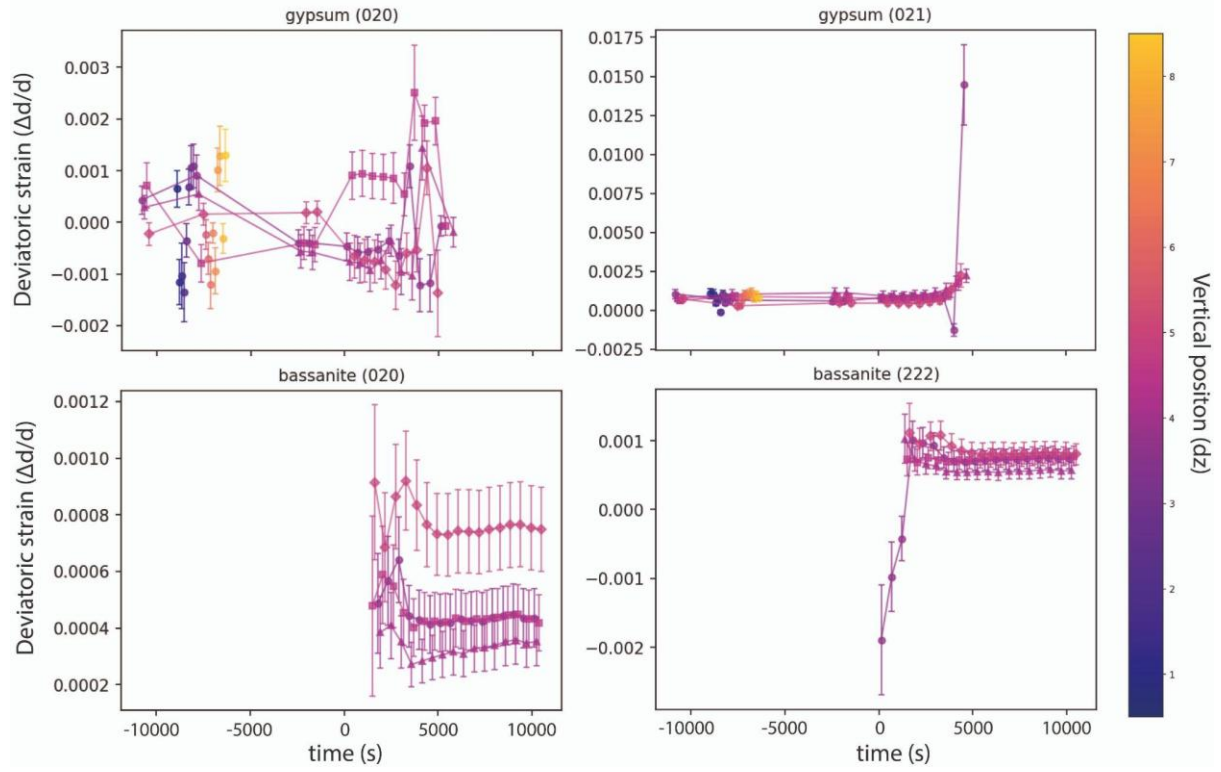


Figure 9 Deviatoric strain during the gypsum-bassanite dehydration reaction inferred from the d -spacing evolution fitted and calculated by CPF. Only two reflections per phase are shown for visibility with gypsum (020) and (021) in the upper panels and bassanite (020) and (222) on the lower panels. The symbol color bar indicates the vertical position in the sample. Time has been set to 0 when the temperature exceeds 100.6C, the estimated phase boundary (see Gilgannon et al. 2023).

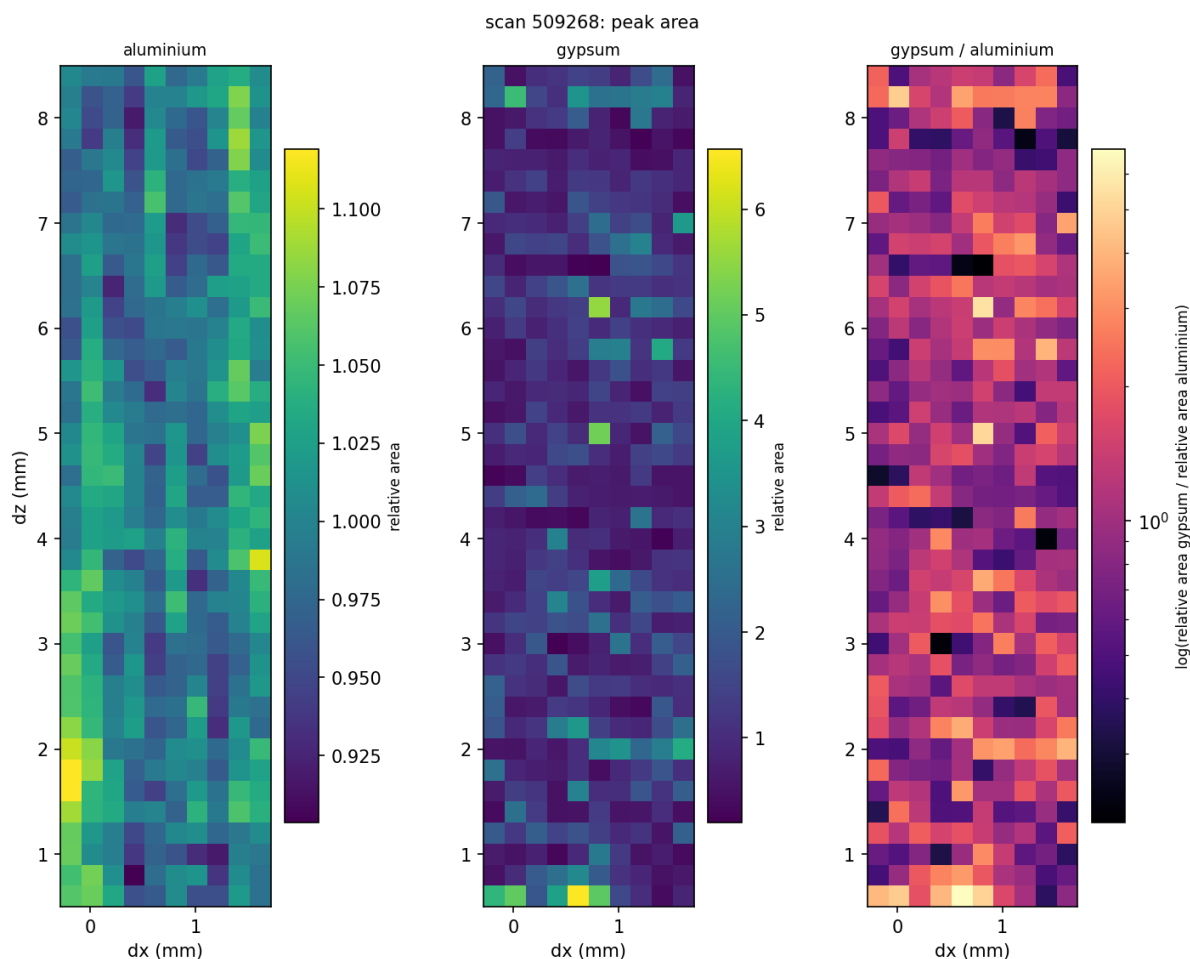


Figure 10 Spatial maps of relative area of fits to (a) aluminium and (b) gypsum diffraction peaks, and (c) the ratio of gypsum / aluminium peak areas (log scale).

Supplementary materials:

Supplementary method S1: Phase proportion extraction from XRD data and Continuous Peak Fit software.

Time-resolved diffraction data were acquired using sweeping acquisitions throughout the dehydration experiments. Prior to peak fitting, sample-detector geometry was calibrated in Dioptas using a LaB_6 calibration standard. Preprocessing consisted of sample to detector distance calibration together with masking the beamstop, detector-module gaps and dead pixels. Preprocessed images were analysed using Continuous Peak Fit (CPF, <https://github.com/ExperimentalMineralPhysics/Continuous-Peak-Fit>, Chen et al., 2021, Daniel et al., 2023 and Zhang et al., 2024), a Python-based repository that fits continuous peak models directly to diffraction images without resampling detector pixels. Diffraction peaks are represented using pseudo-Voigt functions whose parameters are expressed as Fourier series in azimuth, with the order of the series selected according to the complexity of the data.

Peak tracking was performed using the CPF package. Reflections corresponding to the six most intense and best-resolved peaks of the reactant (gypsum) and seven peaks of the product (bassanite) phases were selected for analysis. For each reflection, 2θ ranges were manually defined in order to maximise target peak inclusion while minimising overlap with neighbouring reflections whenever possible. Additional fitting parameters were specified to assist peak fitting convergence.

Prior to batch processing the full time-series, a subset of representative diffraction datasets was used to determine the optimal fitting parameters. The CPF order-search function was employed to evaluate different fitting approaches, including Fourier-series and spline-based representations. These tests were used to identify fitting strategies that balanced fit quality, robustness and computational efficiency.

Once the fitting strategy had been established, all datasets were processed using a custom Python wrapper developed to batch-process CPF fitting and visualise and evaluate results. This is required due to the volume of data generated during this 4D characterisation. For a single dehydration experiment, processing the sweeping scans required 86 CPF fitting runs across 157 scans, resulting in over 2,000 individual peak fits. An automated wrapper for input generation, execution, visualisation and fit-quality control was therefore essential for practical data processing.

When fitting a series of images, CPF uses the previous fit result as initialisation for the next fit, making it robust against minor peak shifting as well as disappearing peaks. For this reason, gypsum reflections were processed in chronological order, as this ordering follows the progressive disappearance of the reactant phase. In contrast, bassanite reflections were processed in reverse chronological order, so that the sequence of fits is applied to peaks decreasing in intensity rather than fitting weak peaks emerging from background noise.

The fitting procedure performed particularly well for intense, sharp and isolated reflections. Greater uncertainty was observed during the final stages of phase disappearance and the earliest stages of product formation, where diffraction peaks approached background-noise levels. Consequently, an additional data cleaning step was required to evaluate and exclude poor fits or fits to absent peaks, which occur wherever the phase amounts fall below the sensitivity for the experiment setup and can vary between reflections and spatial positions. This involved an initial automated flagging of possible poor fits followed by manual inspection of detector data, fit profiles and residuals. Fits affected by poor convergence, severe peak overlap or low signal-to-noise ratios were flagged and excluded from further analysis.

For each successfully fitted reflection, integrated peak areas were extracted at each position and timepoint. These values were normalised relative to a reference scan, which for gypsum was the first scan after crossing the phase boundary between gypsum and bassanite (100.6°C) and the last scan before cooling for bassanite. This normalisation is important because not all reflections for a given phase can be included (due to peak overlap), so calculating a total diffracted intensity per phase would not be feasible, and selected reflections for each phase may have different absolute intensities. Because peak intensities, and therefore integrated areas, may vary with temperature and pressure, reference values were selected under conditions as close as possible to those prevailing during the reaction.

Finally, the relative amount of each phase was estimated by summing the integrated areas of all fitted reflections belonging to that phase and normalising by the corresponding summed reference peak areas. This intensity-weighted averaging over multiple reflections reduced the influence of individual fit uncertainties and local peak-overlap effects, providing a more robust measure of phase evolution throughout the dehydration experiments. A final conversion curve was obtained by renormalising the bassanite summed, normalised areas (phase amount) by the sum of the gypsum and bassanite phase amounts, ensuring that the resulting relative phase fractions remain bounded between 0 and 1.

Supplementary method S2: Strain and stresses from XRD data and Continuous Peak Fit software.

Lattice strain analysis was performed using the Continuous Peak Fit (CPF) software

package. In contrast to conventional approaches, where diffraction rings are first azimuthally segmented ("caked") and individual sectors fitted separately, CPF fits continuous peak models directly on the complete, as-collected, detector pixel array, without resampling, by assuming all peak parameters (e.g. position, height, width) have an azimuthal dependency that is described by a Fourier series. By fitting the full diffraction data simultaneously, CPF exploits a larger fraction of the available diffraction information and generally provides improved fitting stability and lower uncertainties on peak-position determination (see CPF GitHub repository).

Following the detector calibration and masking procedures described in Supplementary Method S1, each reflection was fitted to determine the diffraction-ring geometry and extract the corresponding lattice-strain tensor components from the d-spacing together with fitting residuals and uncertainty estimates.

The resulting lattice strains describe deviations in lattice spacing relative to a reference state and provide a direct measure of the elastic response of the crystalline phase. The quality of the strain determination was evaluated through inspection of fitting residuals, uncertainties and visual examination of fitted diffraction-ring geometries.

Lattice stresses may subsequently be estimated from the measured lattice strains using the relevant elastic properties of the investigated mineral phase. Depending on the level of approximation required, this may involve the use of isotropic elastic constants (e.g. Young's modulus and Poisson's ratio or bulk modulus) or more complete single-crystal elastic tensors. In the simplest case, stress may be estimated through the generalized form of Hooke's law:

$$\sigma = C\varepsilon \text{ (s1)}$$

where σ is stress, ε is lattice strain and C represents the appropriate elastic stiffness coefficients for the phase under consideration.

Supplementary method S3: XRD map data processing and Continuous Peak Fit software.

XRD mapping scans were processed in CPF using an approach similar to that employed for single-point and sweeping analyses. Although the package does not currently accept 2D spatially mapped data collected in a single HDF5 file, extracting the individual scans from a TIFF sequence enables the map to be processed using the standard fitting workflow. Particular attention must be paid to the orientation and ordering of the TIFF files in this configuration.

XRD images were taken at 0.2 mm steps over a 2 x 8 mm area centred on the sample. For each detector image, 6 gypsum and 7 aluminium reflections were fitted. Each reflection's area was calculated using a pseudo-Voigt function and averaged over azimuth.

Post-processing of the fitted maps was performed using our custom wrapper, including the flagging of outliers as described in Supplementary Method S1, followed by the generation of maps of relative peak areas or intensities. Fits were excluded if the peak centre was within 10% of either side of the fitted range or more than 0.15 of the window width from the combined data peak across the full map. Map data are more challenging to process than sweep data because of the large volume of fitting outputs (here 5200 individual fits for 400 individual points) and the more spotty nature of individual acquisitions. Consequently, fitting quality is generally lower and requires careful post-processing examination to identify poor-quality fits. After removal of flagged points, at each position, a reflection's fitted area was divided by its median over the map, and the average of these values was used as the phase amount at that position. The resulting ratio of gypsum:aluminium phase amounts is also displayed as a map. Figure 10 is intended primarily to demonstrate the capability of the mapping and processing workflow, rather than to present a mature scientific interpretation of the spatial variations.

Supplementary method S4: Rietveld refinement analysis

Rietveld refinement of the diffraction data was performed in GSAS-II. Initial instrument parameters were based on the synchrotron geometry exported from Dioptas, using a wavelength of 0.172 Å. A preliminary refinement of a LaB₆ calibration pattern was then performed to obtain more representative starting values for the instrumental profile. In particular, the U, W, X and Y profile parameters and the SH/L asymmetry parameter were refined and subsequently used as initial values for refinement of the sample diffraction data.

The sample diffraction pattern was then imported, together with crystallographic information files for bassanite (CIF 2105042) and aluminium (CIF 9012003). The background was first described using a Chebyshev function and then supplemented by manually defined background anchor points. Manual definition of the background was required because of the additional contribution from the sample jacket. The instrumental profile parameters, including SH/L, were allowed to refine together with the sample data and were iteratively refined until a stable fit was obtained. These parameters remained highly stable, with only limited variation from the values obtained from the LaB₆ calibration.

The aluminium peaks associated with the pressure vessel were refined separately before focusing on the sample phase. The two aluminium contributions from the upstream and downstream sides of the vessel were constrained to share the same refinement parameters. The aluminium lattice parameters, crystallite size and microstrain were then progressively refined, together with the instrumental and profile parameters, until a stable description of the vessel contribution was obtained. Regions containing the aluminium vessel peaks were subsequently excluded from the refinement of the bassanite structure.

Refinement was then focused on the bassanite phase. Parameters were introduced progressively rather than refined simultaneously, with repeated refinement cycles performed after each new group of variables was introduced. The scale factor and lattice parameters were first allowed to refine to establish the phase contribution and reproduce the experimental peak positions. Peak-shape and broadening contributions were subsequently considered, including microstrain, while the instrumental profile parameters initialised from the LaB₆ calibration were allowed to refine. These parameters remained stable and showed only limited variation during subsequent refinement cycles.

Once a stable description of the diffraction profile had been obtained, structural parameters were progressively introduced. Thermal displacement parameters were refined, followed by atomic positions, with successive refinement cycles performed until the solution stabilised. At each stage, newly introduced parameters were assessed from their effect on the calculated diffraction pattern and overall convergence before proceeding to the next group of variables. This sequential approach was used to limit correlations between profile, microstructural and structural parameters. The final refinement therefore incorporated the bassanite scale and lattice parameters, microstrain, thermal parameters and atomic positions, together with the refined instrumental profile and background description.

Supplementary Note S5. Sources of uncertainty and limitations

Several sources of uncertainty affect diffraction measurements performed through miniature triaxial rigs. These uncertainties arise from the diffraction instrumentation, the sample characteristics, the pressure-vessel geometry and the subsequent data-processing workflow. A detailed analysis of uncertainties associated with the Mjölñir and Heitt Mjölñir platform is provided in Freitas et al. (2024) and Gilgannon et al. (2023).

The experimental geometry was calibrated using a LaB₆ standard prior to each experiment. Uncertainties in detector distance, beam centre position and detector orientation

contribute directly to uncertainties in calculated diffraction angles, d-spacings, lattice strains and lattice stresses. For the detector configurations employed in this study, the angular sampling was primarily controlled by detector distance and pixel size, corresponding to an angular resolution of approximately 0.011-0.02° per pixel depending on the detector position.

Potential misalignment of the sample relative to the rotation axis can alter the apparent diffraction geometry and broaden vessel-derived diffraction features during rotational acquisitions.

The diffraction fitting procedure also introduces uncertainty. Continuous Peak Fit (CPF) returns fitted peak positions, peak intensities, peak widths and associated fitting residuals for each analysed reflection. Peak-position uncertainties depend primarily on peak intensity, peak overlap, signal-to-noise ratio and diffraction-ring continuity. Reflections affected by severe overlap, poor convergence or low signal-to-noise ratios were flagged and excluded from further analysis when necessary. However, fitting uncertainties can be calculated and propagated during these fitting steps and are routinely returned by the CPF.

For the phase-evolution analyses presented in this study, uncertainties are additionally associated with fitting uncertainties described above and quantified in CPF. Additional uncertainties can arise from lateral heterogeneity in the sample (which can be checked with vertical profiling and mapping), as well as preferred orientation effects and variable powder statistics.

For stress and strain applications, uncertainties in lattice-strain determination propagate directly into calculated stresses in CPF through the selected elastic model. Additional uncertainty may arise from the choice of elastic constants, assumptions regarding stress state and crystallographic anisotropy. The present study therefore focuses primarily on demonstrating the feasibility of strain measurements through miniature triaxial rigs rather than on providing a complete uncertainty analysis of stress inversion procedures.

Supplementary figures:

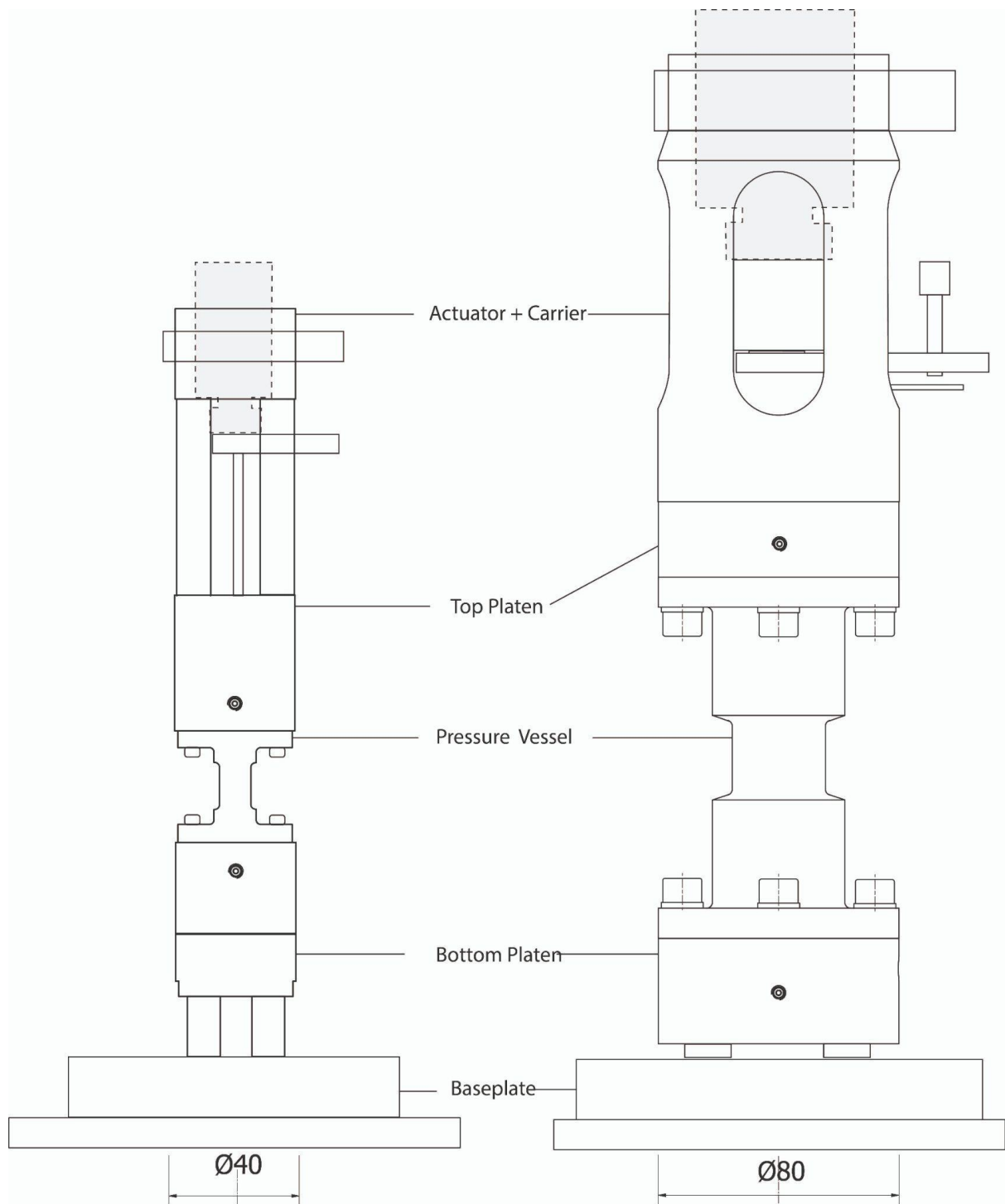


Figure S1 Schematic representation of Mjölhir and Heitt Mjölhir devices with labelled components.

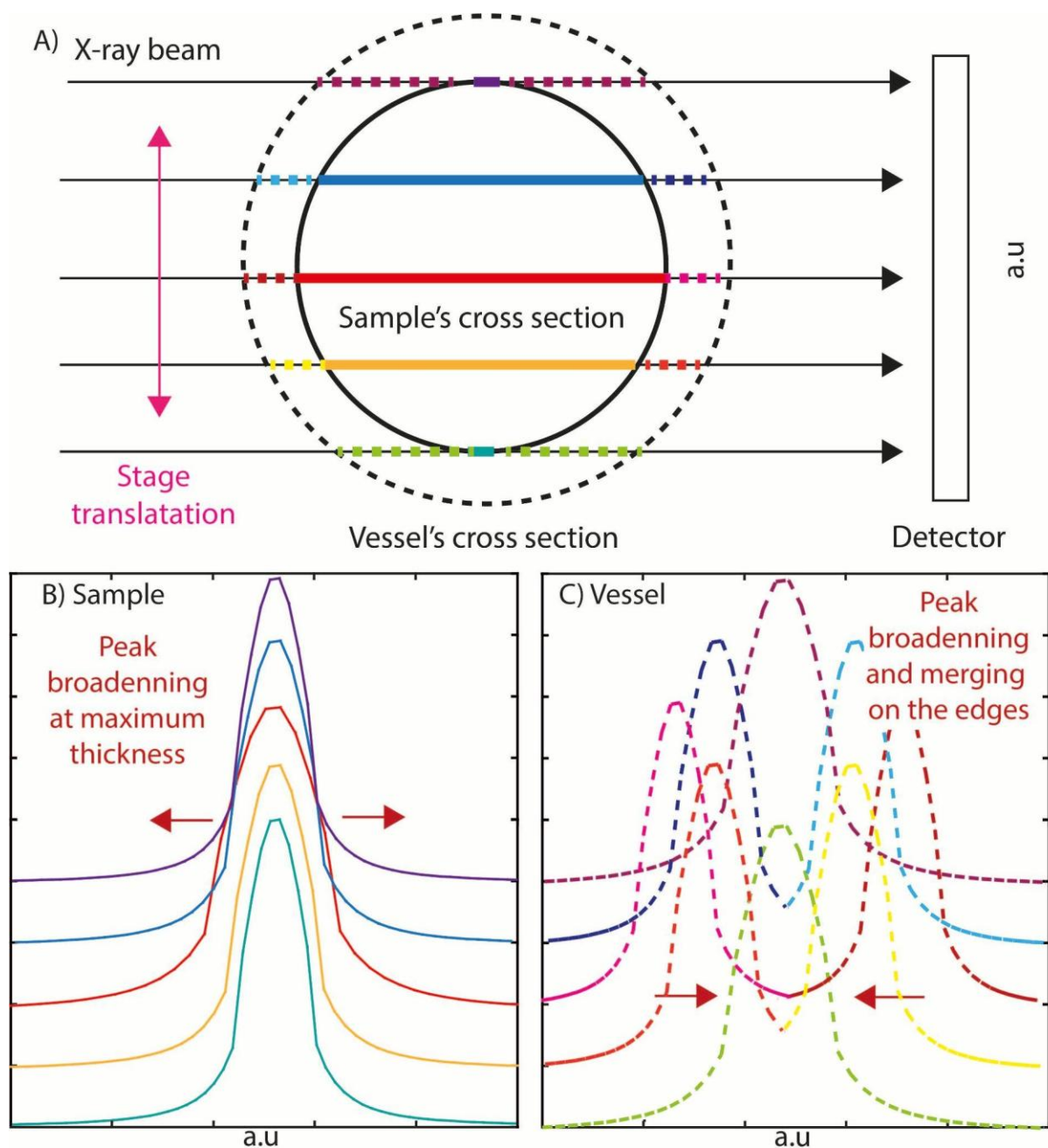
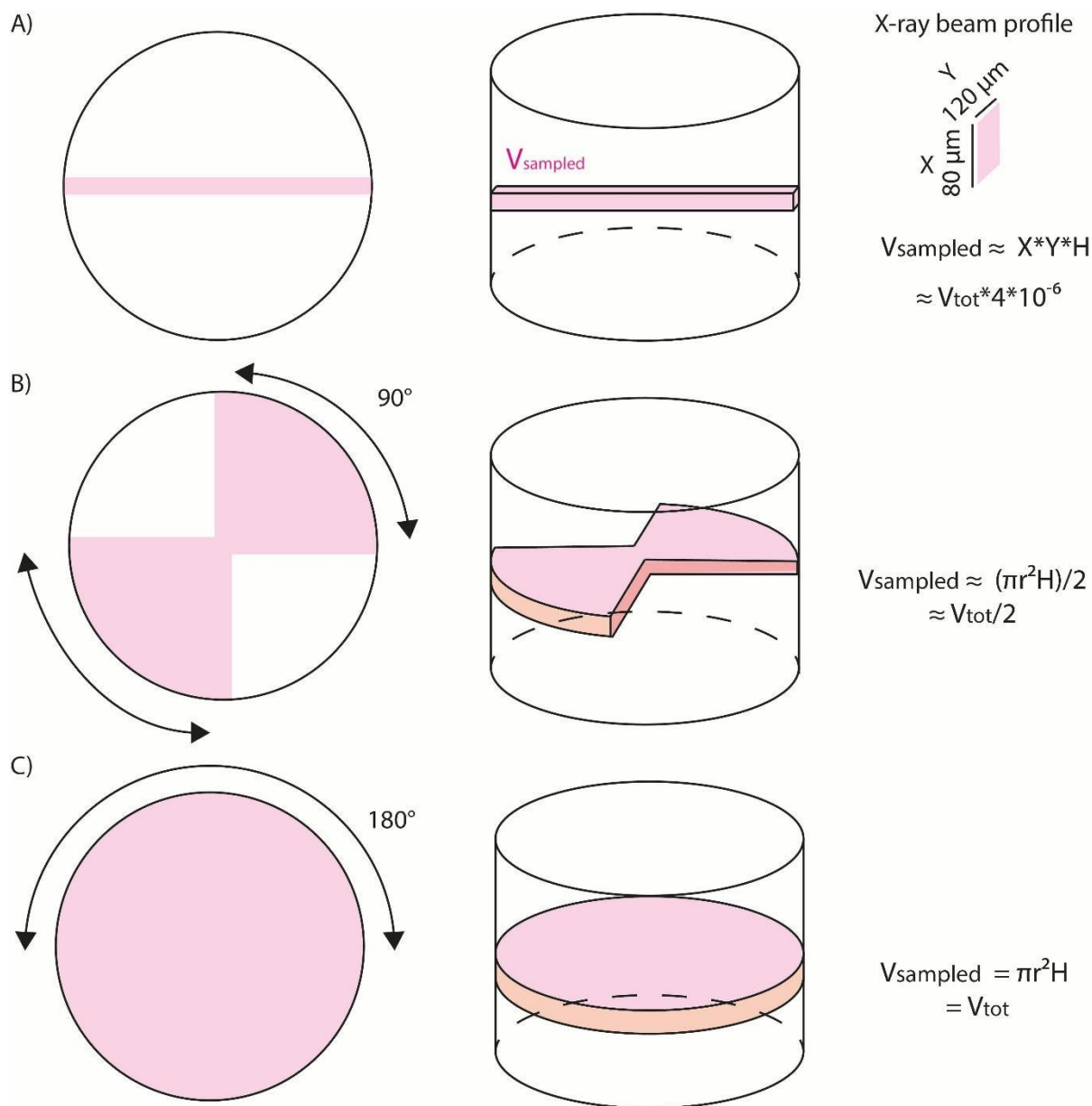


Figure S2 (A) Schematic illustration of variations in beam path length through a cylindrical specimen. The effective sample thickness intersected by the X-ray beam varies with beam position, both during diffraction mapping and when the specimen is not perfectly centred on the rotation axis. The maximum path length occurs through the specimen centre (red) and decreases progressively towards the specimen edge (purple and green). (B) Corresponding conceptual representation of geometric peak broadening. As the beam path length increases, diffraction arises from a larger range of sample-to-detector distances, increasing the geometric contribution to peak width. Broadening is greatest when the beam traverses the full specimen diameter through the rotation axis (see Equations 7 & 8). Consequently, accurate sample centring is essential for minimising geometric broadening and obtaining optimal angular resolution.



Not to scale

Figure S3 Conceptual illustration of the sample (of radius r) volume interrogated by a beam of height H and width Y . (A) Static single-point acquisition, where diffraction originates from a fixed illuminated volume. (B-C) Rotational acquisitions (rocking or sweeping), shown at two different angular positions, illustrating how specimen rotation progressively brings additional crystallites into diffraction condition while maintaining the same beam position within the sample.

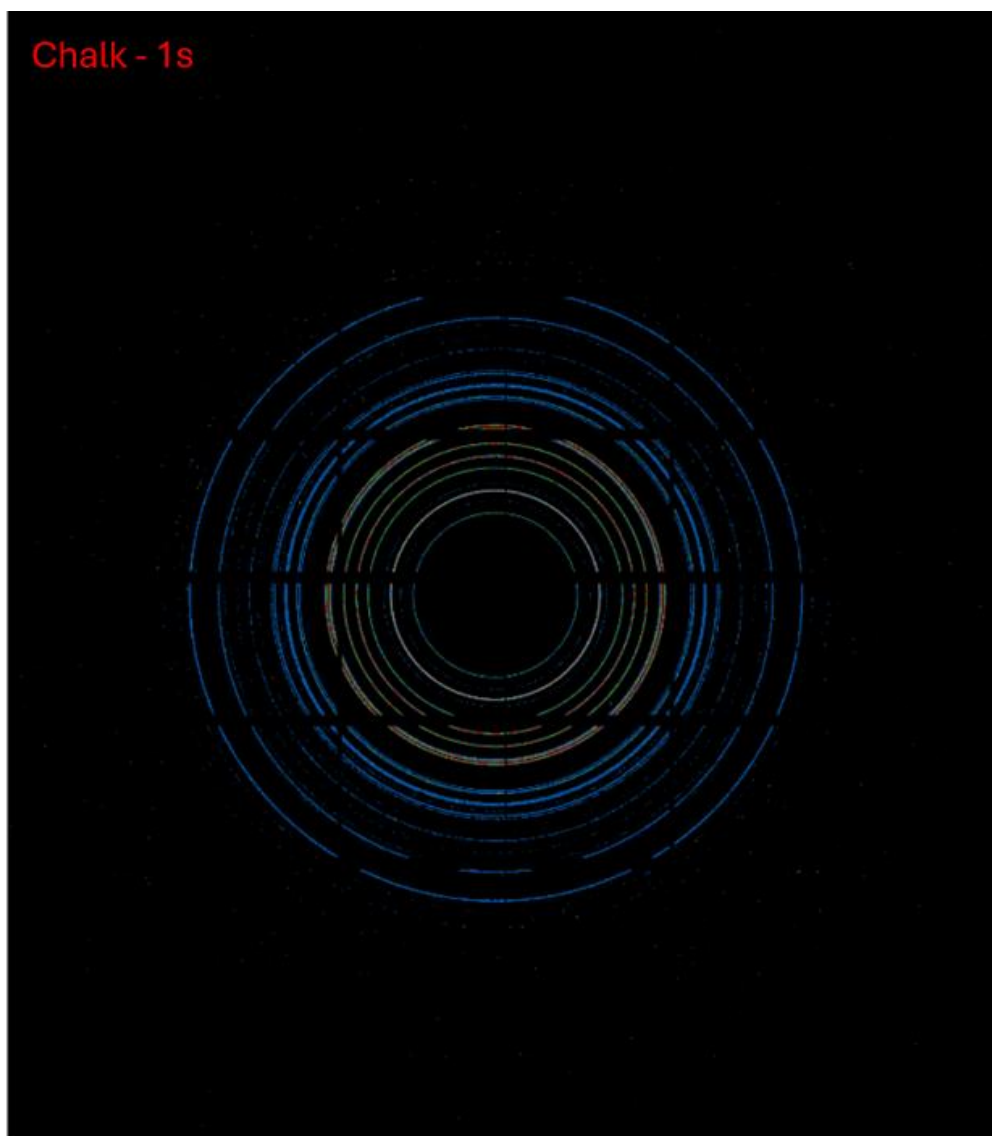


Figure S4 2D area diffractogram of chalk sample (mostly calcite) with 1 second exposure. The resulting pattern approximates ideal powder diffraction for a fine-grained sample.

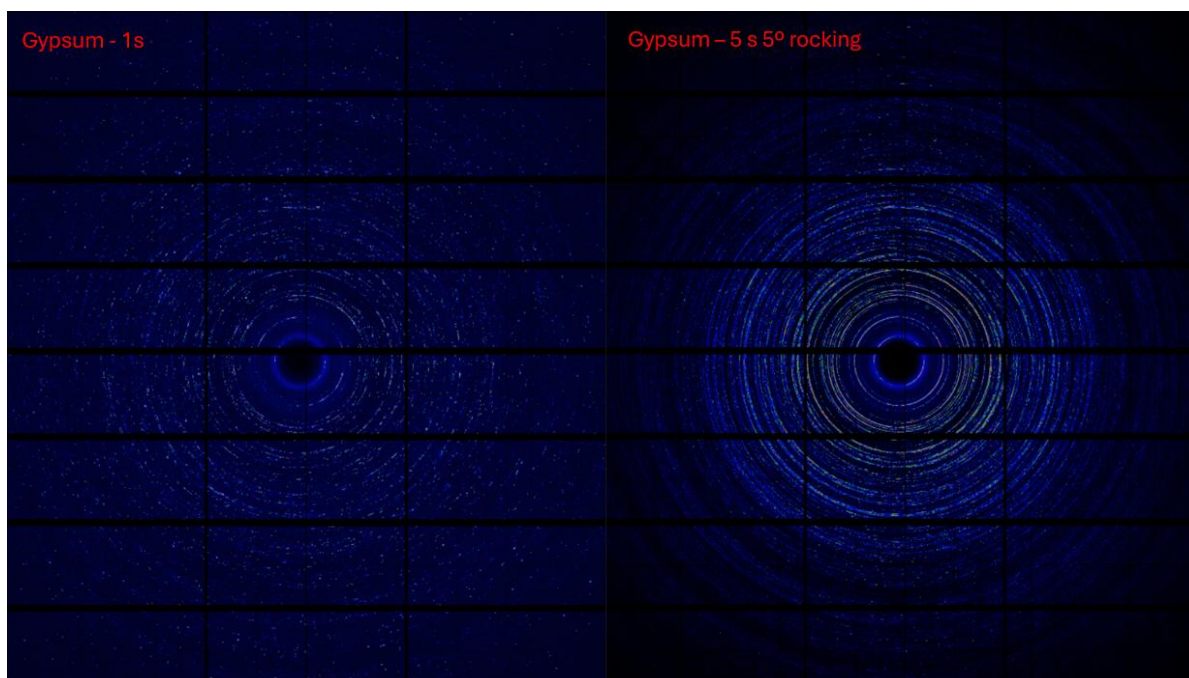


Figure S5 2D area diffractograms of Volterra Alabaster gypsum sample (mostly gypsum and some celestite) with 1 second exposure on the left and 5 s exposure and 5° rocking on the right. The 1 second exposure (left) reflects a high spottiness of the recovered patterns (due to coarser grain size than chalk specimen in figure S4) while rocking acquisition generates diffraction rings which are much closer to the ideal powder diffraction.

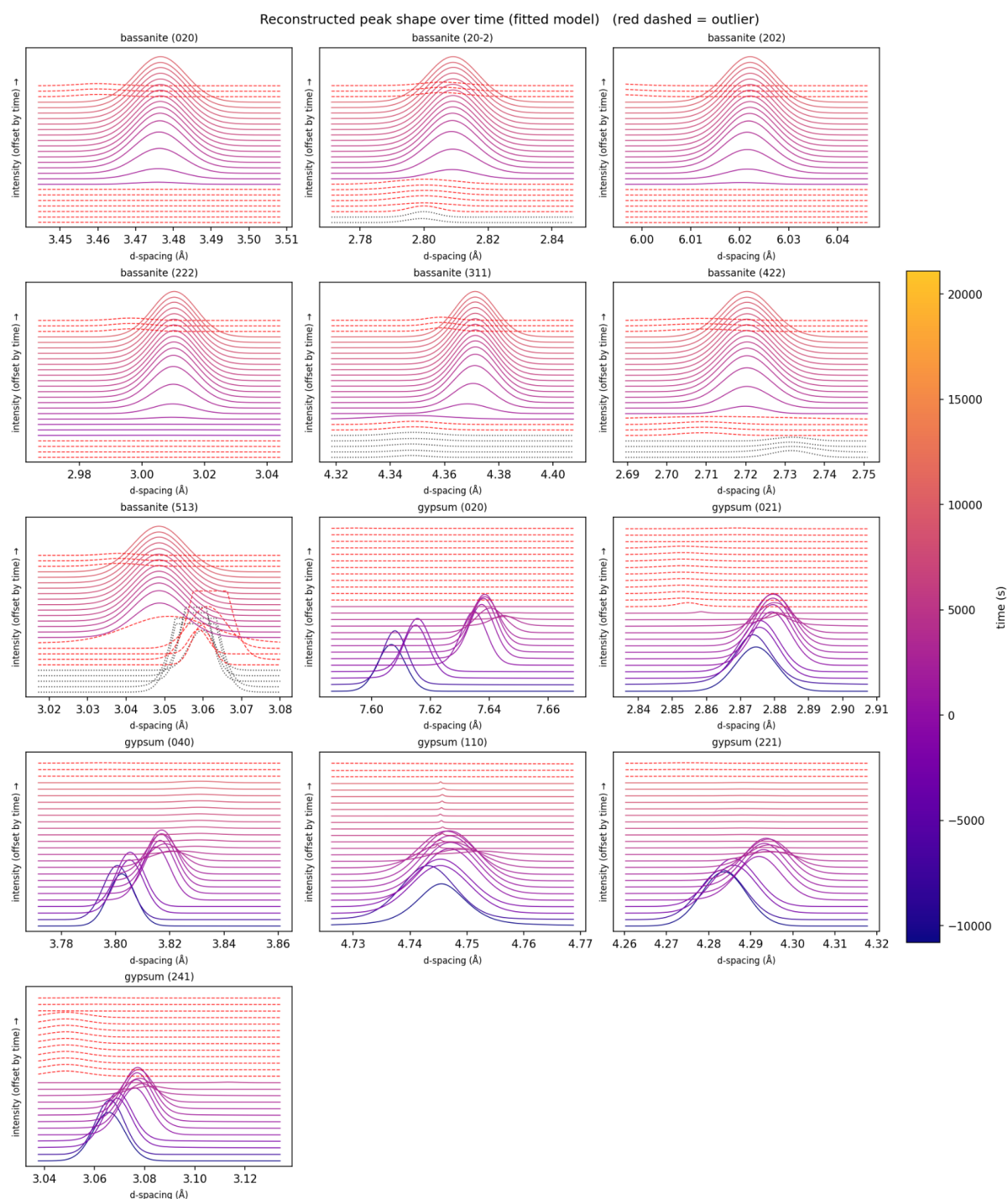


Figure S6 Evolution of the principal reflections of the reactant phase (gypsum) and product phase (bassanite) during the in-situ dehydration reaction for a fixed vertical position (3.7 mm from top interface) and using sweeping analyses (90° angle). Continuous Peak Fit (CPF) analysis was performed on the 2D diffraction images, and the resulting fitted peak profiles are shown here as azimuthally integrated 1D representations plotted as a function of d-spacing. Time zero corresponds to the intersection of the experimental temperature path with the gypsum-bassanite phase boundary. Red dotted traces indicate fits excluded from subsequent analysis due to low signal-to-noise ratios or the appearance of additional reflections that prevented reliable fitting.

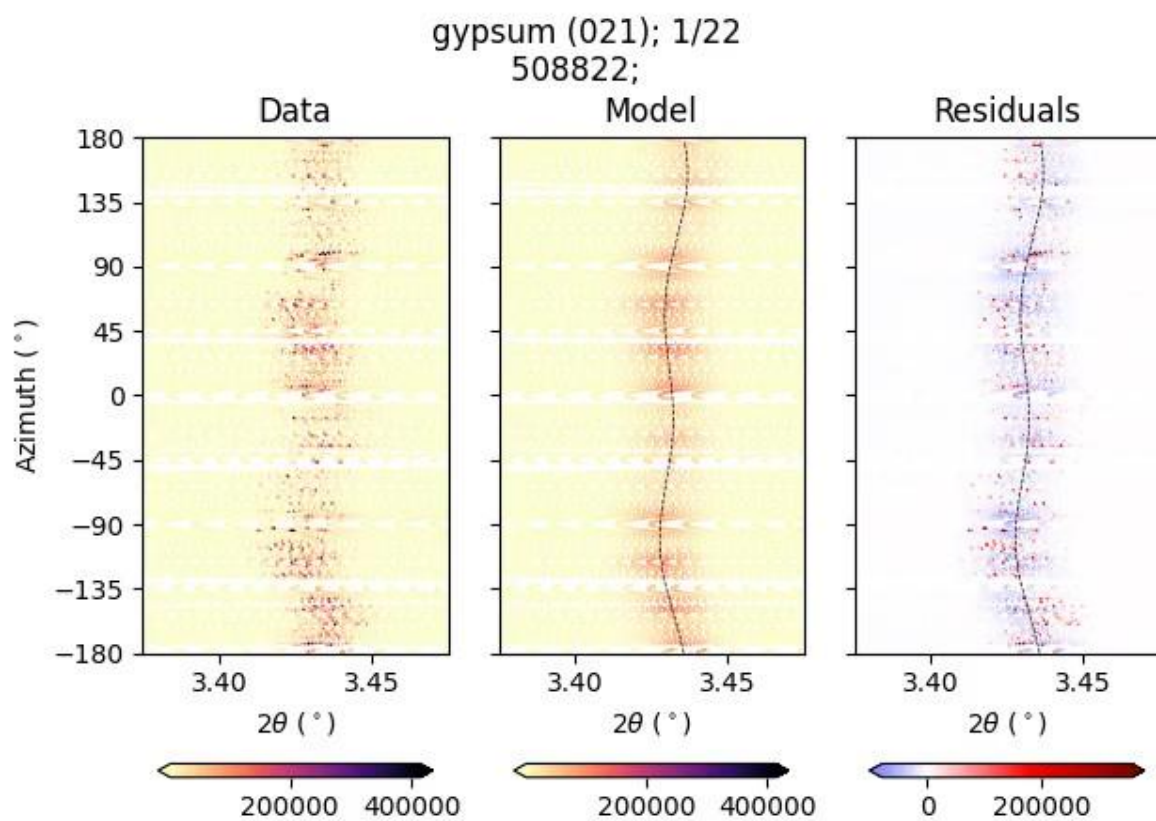


Figure S7 Azimuthal variation of the gypsum (021) reflection in 2θ (from a 90° sweeping acquisition at one vertical position $dz=3.7$ mm). The azimuthal representation shows the undulatory variation in peak position associated with lattice strain.