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## Abstract

Crystallographic parameters serve as fundamental archives of crystallization environments, with pressure generally acting as a key variable governing crystal formation. In magmatic systems, tracking crystallographic and chemical parameters in clinopyroxene is critical for robust magmatic thermobarometry and reconstructing crystal life histories. While chemical thermobarometry is limited by melt dependencies, crystallographic alternatives with the measurement of lattice parameters have historically faced significant analytical barriers too. Specifically, traditional single-crystal X-ray diffraction (SC-XRD) relies on averaging bulk crystal fragments (>40–50  $\mu\text{m}$ ) and cannot resolve the intra-crystalline crystallographic zoning necessary to decouple pressure-induced contraction from localized chemical substitutions. Here, we present synchrotron-based X-ray microdiffraction (s- $\mu\text{XRD}$ ) coupled with a suite of micro-analytical tools ( $\mu\text{-XRF}$ , EPMA, SC-XRD) and applied to clinopyroxene experimentally crystallized at 0.001 to 35 kbar and 1000 to 1200  $^{\circ}\text{C}$ . During s- $\mu\text{XRD}$  analyses, a fixed-stage energy-scanning setup (13.2–22.0 keV) captured micrometer-resolution, 3D reciprocal-space diffraction data for clinopyroxene within multiphase charges.

The obtained datasets is complex and heavy (multi-gigabyte) and we developed a well-structured automated computational workflow integrating: (1) localized diffraction features and vectorization across energy steps; (2) phase segmentation using  $\mu\text{XRF}$  elemental masks (Ca, Cr, and Ca/Fe ratios); (3) density-based spatial clustering (DBSCAN) in reciprocal space; and (4) pixel-by-pixel non-linear least-squares refinement of monoclinic (C2/c) lattice constants constrained by at least 30 robust anchor reflections.

Our results demonstrate that while strongly zoned samples yield crystallographic questionable bulk values via SC-XRD, s- $\mu$ XRD explicitly resolves distinct core and rim unit-cell volumes and  $\beta$  angles. In 15 kbar crystals, s- $\mu$ XRD decouples a constrained core (cell volume between 433.45-435.32 Å<sup>3</sup>) from a more variable rim (432.88-436.78 Å<sup>3</sup>), correlating with localized variations in jadeite and wollastonite. Unlike bulk-averaging SC-XRD, s- $\mu$ XRD isolates distinct crystallographic domains by quantifying unit-cell volumes at the micron scale. This in-situ approach preserves spatial context, allowing estimation of lattice parameters from discrete cores and rims. This technique provides a transformative pathway to refine thermobarometric models in dynamic volcanic systems, offering a robust analytical framework for deciphering complex open-system magma plumbing architecture and the localized physicochemical triggers governing orthomagmatic ore deposit formation.

## 1. Introduction

Crystallographic parameters fundamentally record the physicochemical conditions dictating mineral formation, cooling history and secondary evolution (Angel et al., 2022; Murri et al., 2018; Nimis, 1995; Ye et al., 2026). Variations in pressure and temperature involve direct thermo-mechanical strain on mineral structures, systematically impacting crystallographic parameters such as unit-cell volume,  $\beta$  angle, and M1/M2 polyhedral geometries in a variety of magmatic minerals (Dal Negro et al., 1989; Morfin et al., 2024; Pamato et al., 2019). While this fundamental principle could be used to indirectly estimate important parameters such as pressure of mineral formation, relying on these crystallographic parameters variations as precise barometers presents a significant analytical challenge. Crystallographic parameters are not solely controlled by pressure and temperature; they are also strongly influenced by the internal chemical composition of minerals (Murri et al., 2016). Consequently, developing accurate thermobarometric models based on crystallographic parameters requires high-resolution techniques capable of decoupling the microstructural and chemical variations.

Clinopyroxene is a monoclinic mineral widely distributed across a broad range of geological settings and formation depths. While it is commonly found in igneous magmatic systems (i.e., alkaline, mafic to ultramafic; Macdonald et al., 2023; Schoneveld et al., 2020), it also crystallizes in high-pressure metamorphic environments (i.e., eclogite and blueschist; Vanandois et al., 2022), and metasomatic-hydrothermal systems (skarns; Hantsche et al., 2021). Clinopyroxene chemistry and crystal structure record a large diversity of physicochemical changes that occur during magmatic processes, commonly marked by zoned textures (i.e., core-mantle-rim textures; Macdonald et al., 2023; Schoneveld et al., 2020). The chemistry of

clinopyroxene is widely utilized to estimate pressure and temperature through various thermobarometers models, relying on in-situ and mapping micro-analyses (Ágreda-López et al., 2024; Neave and Putirka, 2017; Putirka et al., 1996). However, the composition of clinopyroxene is strongly dependent on the composition of the co-existing crystallizing melt, which can limit the accuracy of existing thermobarometry models (Neave and Putirka, 2017). Studying crystallographic parameters of clinopyroxene may be particularly critical for refining existing chemically based thermobarometers and better understanding magmatic processes (Nestola et al., 2007; Nimis, 1995; Tommasini et al., 2022).

Estimating pressure using clinopyroxene crystallographic parameters has traditionally relied on ex-situ single-crystal X-ray diffraction (SC-XRD; Dal Negro et al., 1989; Nimis and Ulmer, 1998). Single-crystal XRD measures 3D reflection patterns from a single crystal fragment ( $>50\text{ }\mu\text{m}$ ) using a monochromatic beam with a spatial resolution typically yielding  $100\text{--}200\text{ }\mu\text{m}$  to determine bulk crystallographic parameters. Pioneering researches on clinopyroxene (e.g., Dal Negro et al., 1982; Nestola et al., 2007; Nimis, 1995) have demonstrated that specific metrics, such as unit-cell volume and M1 site volume, broadly vary with pressure. Unfortunately, standard SC-XRD methods cannot account for intra-grain crystallographic parameter variations, resulting in large errors on the measurements ( $\sim > 2\text{ kbar}$ ; Nimis, 1995). High spatial resolution is critical because crystallographic parameters also respond to localized compositional variations, most notably the pressure-sensitive jadeite component (Nestola et al., 2007; Nimis and Ulmer, 1998).

This study addresses this knowledge gap by applying synchrotron-based X-ray microdiffraction (s- $\mu$ XRD) to clinopyroxenes experimentally synthesized between  $0.001\text{--}15\text{ kbar}$  and  $1000\text{--}1200\text{ }^{\circ}\text{C}$ . To our knowledge, these are the first XRD

measurements of experimentally synthesized clinopyroxenes using a natural microbasaltic starting material. The energy-dispersive s- $\mu$ XRD mapping provides the microscale spatial resolution necessary to quantify crystallographic parameters variations within thin sections, overcoming the challenges of analyzing complex multiphase experimental or natural assemblages (e.g., containing olivine and amphibole). To generate a comprehensive crystallographic and chemical dataset, in-situ s- $\mu$ XRD was coupled with EPMA and  $\mu$ XRF mapping on the same samples and integrated with SC-XRD measurements on clinopyroxene.

## **2. Analytical and computational methods**

### **2.1. Sample preparation**

The analyzed samples consist of experimentally crystallized microbasalt charges (App. 2) synthesized at ETH Zurich, utilizing high-pressure and high-temperature protocols (see Ulmer, 1989; Ulmer et al., 2018 for further details). The experimental samples suite covers pressures from 0.001 to 35 kbar and temperatures from 1000 to 1200 °C (full experimental conditions are provided in App. 2). A wide formation pressure range with limited temperature variations was selected to systematically evaluate pressure effect on clinopyroxene crystallographic variations (Table 1).

Following rapid quenching of the piston-cylinder assemblies, the graphite–Pt capsules were mechanically broken to extract the crystallized charges. Rather than polishing the capsules longitudinally, intact chunks of the experimental charges were extracted, embedded in epoxy, and securely glued onto glass slides. The mounted chunks were then ground and polished down to a standard petrographic thin-section

thickness of 30  $\mu\text{m}$ . Crucially, prior to the synchrotron X-ray microdiffraction (s- $\mu\text{XRD}$ ) measurements, the 30  $\mu\text{m}$ -thick sample sections were deliberately detached from their glass slides. Removing the sample from the glass backing is essential for transmission-geometry analyses to prevent geometric artifacts, shadowing, and the intense amorphous background scatter that would otherwise be generated by the glass substrate.

Samples were partitioned based on the two XRD techniques performed (Table 1): in-situ s- $\mu\text{XRD}$  mapping (Fig. 1) specifically targeted the low-pressure (0.001 kbar) PU354 and the high-pressure (15 kbar) PU143 samples. Complementary ex-situ single-crystal XRD (SC-XRD; Fig. 1) was conducted on isolated, high-quality crystal fragments extracted from a broader suite of samples, including the 7.5 kbar (PU189), 10 kbar (PU178), and 35 kbar (PU158) samples crystallized at relative similar temperature (1000-1200  $^{\circ}\text{C}$ ). Depending on the specific P-T conditions (Table 1), the experimental charges produced diverse multiphase assemblages. Clinopyroxene (cpx) consistently crystallized as a primary phase, coexisting with varying modal proportions of quenched melt (L), olivine (ol), plagioclase (plag), and spinel (sp) at lower pressures (e.g., samples PU354). At intermediate to high pressures (7.5 to 35 kbar), the phase assemblages progressively incorporated orthopyroxene (opx), amphibole (amph), ilmenite (ilm), and ultimately garnet (gar) in the highest-pressure runs (PU158).

## **2.2. Petrography and EPMA mapping**

Initial optical microscopy identified clinopyroxenes-rich zones and assessed mineral phase distribution and grain size. For each sample, three representative areas were selected for electron probe microanalysis (EPMA) mapping on a JEOL JXA-

iHP200F hyperprobe (Department of Earth Sciences, University of Geneva). We acquired backscattered electron (BSE) images and elemental intensity maps to identify compositional zoning, and subsequently processed these elemental maps in XMapTools (Lanari et al., 2014) to produce mineral phase maps using the Random Forest algorithm (Lanari and Tedeschi, 2025; Fig. 2). Details about the analytical EPMA methodology is provided in Appendix-2.

### **2.3. Single-crystal XRD analyses**

Single-crystal XRD (SC-XRD) measurements were performed at the Laboratory of Crystallography, at University of Geneva, using an XtaLAB Synergy-S diffractometer equipped with a hybrid pixel array “hypix arc 150” detector and a microfocus sealed tube (PhotonJet Cu[K $\alpha$ ] X-Ray source, beam size 200  $\mu$ m). Computing data collection, cell refinement and data reduction were performed using CrysAlisPro© system and software. The structures were solved by using dual-space methods (ShelXT)LG1. Full-matrix least-square refinements on F2 were performed with SHELXLLG1-LG2 and all other calculations were performed with OLEX2LG3 program. A summary of data collections and crystal structure refinements for PU178, PU189 and PU158 is presented in App. 2. In all structures, mixte site occupancies M1 and M2 sites were refined independently with atomic Ca/Mg mixture for M1 and a Fe/Mg mixture for M2. The chemical composition has been constrained to the most abundant elements identified in the EPMA spot analyses. Silicon (tetrahedral site) was kept fully occupied due to the poor Al/Si discrimination with this technique. Chemical compositions and site volumes for PU178, PU189 and PU158, are listed in App. 2.

Studied experimental samples generally contain very tiny crystals, reaching rarely more than 50  $\mu$ m. Conventional SC-XRD measurements were performed

exclusively on samples containing suitably large (mean size from 20 to 40  $\mu\text{m}$ ) and abundant clinopyroxene (>15 vol%; PU189, PU178, and PU158; Table 1), which crystallized at 7.5–35 kbar and 1000–1200  $^{\circ}\text{C}$ . Samples with clinopyroxene falling below conventional detection thresholds (<5 vol% abundance; <20  $\mu\text{m}$  clinopyroxene grain size) were exclusively analyzed using synchrotron-based XRD.

## **2.4. Synchrotron-based XRD analyses**

### **2.4.1. Setup & acquisition**

Data acquisition was conducted at the Submicron Resolution X-ray Spectroscopy (SRX) beamline at the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory. The incident monochromatic X-ray beam was focused to a sub-micron spot size of approximately  $430 \times 450 \text{ nm}$  using Kirkpatrick-Baez (KB) mirrors (Fig. 1). To capture the diffraction signal, a Dexela 2D flat-panel area detector was positioned downstream in transmission geometry (Fig. 1). During the experimental campaign, the sample-to-detector distance was dynamically evaluated and adjusted from an initial 50 mm up to 200 mm. This adjustment was necessary to optimize reciprocal space coverage while mitigating detector saturation from highly intense reflections at specific energy levels. The instrumental control and automated mapping routines were orchestrated using the open-source Python-based Bluesky data collection framework (Allan et al., 2019). Prior to mapping, preliminary X-ray fluorescence ( $\mu\text{-XRF}$ ) fly-scans were used to locate clinopyroxene grains. The incident X-ray beam intensity was then carefully optimized using SR570 current preamplifiers. Amplifier sensitivities were tuned with the beam on to maintain target count rates between  $1 \times 10^6$  and  $2 \times 10^6$ , ensuring the signal remained below the

saturation threshold of  $1 \times 10^7$ . Input offset currents were subsequently optimized with the beam off to a few hundred counts. To account for ambient detector noise and ensure accurate background subtraction during data reduction, blank dark-field images were systematically collected with the beam shutters closed immediately prior to each mapping sequence.

An energy dispersive method was used to capture the complete 3D reciprocal space without the need for mechanical sample rotation (Kämpfe et al., 2005). The incident monochromatic X-ray energy systematically stepped down from a high energy of 22.0 keV down to 13.2 keV. It was executed in consecutive batches using dynamically defined energy arrays. Depending on the required spectral resolution for a given region, the automated script stepped down the beam energy either in broader 0.2 keV intervals (yielding 5 discrete energy slices across a 0.8 keV window, e.g., 22.0, 21.8, 21.6, 21.4, and 21.2 keV) or in finer 0.05 keV intervals (yielding 20 discrete energy slices across a 0.95 keV window). At each precise energy step, a complete spatial raster map was collected using a continuous-motion "scan-fly" technique across the region of interest. Both coarse maps (with step sizes of 1.5-7.5  $\mu\text{m}$ ) and high-resolution maps (with step sizes of 0.3-1.0  $\mu\text{m}$ ) were acquired depending on the required coverage and target grain size. For high-resolution analysis, the raster grids were continuously scanned across the grains with a standard detector dwell time of 0.1 s per pixel.

#### **2.4.2. Localized diffraction detection and map stacking**

Individual energy-specific XRD maps can reach up to 18 GB, posing a significant computational challenge when stacking the required 30–50 maps covering

all the energy acquired. Then, XRD maps were processed in Python using the “xrmaptools package” (Musterman, 2024), which provides specialized tools for loading, correcting, analysing, and visualizing X-ray diffraction mapping data. The XRDMAP and XRDMAPStack classes organize detector images according to sample position and energy, while integrated functions support diffraction-blob detection, data vectorization, map alignment, reciprocal-space analysis, and three-dimensional spot identification. Therefore, this package provides a computational framework for converting the raw detector images into spatially resolved, energy-dependent diffraction data.

For a single XRD map acquired at a specific energy (Fig. 3), each detector image is processed independently to identify localized diffraction features, or “blobs”, while reducing the influence of background noise (Fig. 3A-C). In this script, blobs are detected using the feature “find\_blobs”, including various parameters: (i) minimum filters applying Gaussian smoothing and a window size of 3 pixels. This processing helped suppress isolated noise while retaining coherent intensity regions; (ii) the “multiplier setting” controls the detection threshold: blob features must exceed local background noise thresholds to be classified as significant. After detection, a ~ 10 pixel bounding region is created around each blob to ensure all surrounding intensity belonging to that diffraction feature is included (i.e., red circles in Fig. 3C). Detector-edge pixels are excluded because filtering can produce unreliable features there. The resulting “blob\_masks” identify the selected detector pixels, which are then used to generate the stacked blob image and to vectorize the diffraction data for every map position.

Following blob detection on the series of XRD maps acquired at different energies over the same sample region, the maps are loaded into a XRD map stack

and automatically ordered according to their energy (Fig. 3D). Before stacking, interpolating maps position is computed which establishes a common spatial coordinate grid for the maps using their potential relative shifts. It allows equivalent sample pixels to be compared across the full energy series. Then, the “vectorization step” combines the data from each spatial pixel into a single vector containing the reciprocal-space information and intensity measured at each energy (Fig. 3E). This produces a three-dimensional dataset in which the two spatial dimensions describe the sample position and the third dimension represents the energy-dependent diffraction response. The stacked data are then searched for diffraction features with the “find.3D\_spots” command, using an absolute intensity threshold (abs\_int\_cutoff) and a maximum reciprocal-space distance used to group nearby points into the same diffraction spot (nn\_dist). This step detects significant intensity features in reciprocal space, groups nearby reciprocal-space points into individual diffraction spots, and records their intensity, scattering vectors ( $q_x$ ,  $q_y$ ,  $q_z$ ), scattering vector magnitude ( $q_{mag}$ ), and original map coordinates (Fig. 3E; App. 1). At this stage, no crystallographic reference unit-cell or other lattice parameters are required; the procedure is purely experimental and data driven.

### **2.4.3. Phase deconvolution and ROI**

Experimental samples measured with the synchrotron-based XRD are composed of various minerals phases co-existing with clinopyroxene, such as olivine, amphibole, plagioclase, spinel, and glass, depending on the specific sample. To successfully distinguish the target clinopyroxene phase from associated minerals,  $\mu$ -XRF measurements were acquired simultaneously and in the exact same spatial zone as the synchrotron-based XRD. Raw elemental intensity  $\mu$ -XRF maps (e.g., Ca, Fe,

Cr; Fig. 2) are first geometrically aligned and interpolated to match the spatial coordinates of the X-ray diffraction (XRD) grid. A multi-element mask is subsequently generated to decouple clinopyroxene from the co-existing mineral phases. Specific compositional thresholds (such as minimum cutoffs for Ca intensity, Ca/Fe ratios, and Cr intensity; Fig. 2) were applied to chemically isolate and visualize the clinopyroxene domain. This defined a highly precise and adaptable spatial region of interest (ROI) for subsequent XRD analysis to minimize the interference from deeper inclusions in standard 30- $\mu\text{m}$  thick samples.

#### ***2.4.4. Reciprocal space clustering and reflection indexing***

In this isolated subset, Density-based spatial clustering of applications with Noise (DBSCAN) is executed in reciprocal space ( $q_x$ ,  $q_y$ ,  $q_z$ ) to aggregate individual diffraction spots into discrete, unique physical reflections. Unlike other partitioning algorithms that require a pre-defined number of clusters, DBSCAN relies on a maximum reciprocal distance threshold (i.e.,  $\epsilon = 0.04 \text{ \AA}$ ) and a minimum required number of spots per reflection (min\_samples fixed at 15). This makes it particularly effective for identifying complex, arbitrarily shaped diffraction topologies typical of geological samples while robustly isolating true Bragg reflections from background noise. Once clustered, the algorithm calculates the spatial centroid of each peak to determine its mean d-spacing and integrates the grouped spots to yield the total reflection intensity. A: 3D reciprocal-space ( $q_x$ ,  $q_y$ ,  $q_z$ ) DBSCAN map can be visualized to evaluate the distribution of the clusters and the rejected noise spots (Fig. 4A).

Following peak extraction, a global pre-refinement is performed to calibrate the baseline unit-cell before localized mapping. This baseline is first estimated using equation of Morrison et al. (2018) broadly correlating clinopyroxene chemistry and lattice parameters. This step begins by generating a theoretical reference matrix of interplanar d-spacings based on initial structural guesses, strictly applying the systematic extinction rules for the clinopyroxene C2/c space group (e.g., rejecting reflections where  $h+k$  is odd; Hahn, 2005). Extracted experimental peaks are matched to this theoretical matrix and a 5% tolerance check is fixed (Fig. 4B). High-quality, confidently indexed peaks are what the algorithm will feed into the least-squares minimizer to optimize the bulk unit-cell parameters in the next step.

The bound, non-linear least-squares minimization is applied to the bulk dataset, minimizing the residuals between the calculated and observed d-spacings. This step estimates and optimizes the average monoclinic unit-cell parameters ( $a$ ,  $b$ ,  $c$ ,  $\beta$ ) for the specific sample. The bounds are critical and restrict the minimizer to realistic ranges (e.g., forcing  $a$  to stay between 9.3 and 10.0 Å). It prevents the algorithm from finding a mathematically perfect but physically impossible crystal structure. If the minimizer successfully converges on a solution, it overwrites the initial baseline unit-cell values with the newly optimized sample-specific values.

Then, the optimized unit-cell parameters are used to regenerate a highly accurate theoretical HKL matrix, strictly matching the clinopyroxene C2/c systematic extinctions. All experimental diffraction peaks are then re-indexed against this tailored reference to clear any initial indexing ambiguities. To ensure mathematical stability and prevent misindexing during the computationally intensive spatial mapping phase, a "gold standard" subset of reflections is isolated using intensive structural criteria. More specifically, the algorithm filters out weak or ambiguous data by retaining only

those peaks that encompass: (i) a minimum of individual diffraction spots per map (typically 50-300 diffraction spots depending on the ROI size); (ii) an indexing residual of less than 0.02 Å (Fig. 4C). From this rigorously filtered dataset, up to 30 reflections are extracted to serve as fixed crystallographic anchors. Confining refinement to these anchor peaks guarantees that the mapped lattice variations are driven by diffraction signals rather than noise.

A localized pixel-by-pixel refinement is executed to capture micro-scale crystallographic variations across the mapped grid. Restricted strictly to the chemically defined region of interest (ROI), the algorithm extracts the exact experimental d-spacings of the robust anchor reflections at each individual spatial coordinate. A bounded non-linear least-squares minimization is then applied independently to each pixel, utilizing the previously optimized bulk unit-cell as the initial starting parameter. This continuous spatial optimization dynamically resolves the localized monoclinic lattice parameters ( $a$ ,  $b$ ,  $c$ ,  $\beta$ ) and total unit-cell volume ( $V$ ) for every discrete micro-domain. Simultaneously, the goodness-of-fit at each coordinate is validated by calculating a local R-factor, defined here as the mean absolute percentage error between the experimentally observed ( $d_{\text{obs}}$ ) and theoretically calculated ( $d_{\text{calc}}$ ) interplanar spacings. The resulting localized parameters are compiled into two-dimensional matrices, yielding high-resolution spatial maps of lattice distortions and volume fluctuations that can be directly integrated with chemical zoning profiles.

#### **2.4.5. Visualization, clustering, and dataset export**

This workflow integrates processed crystallographic data with the initial chemical data to produce a comprehensive suite of diagnostic visualizations. High-resolution spatial heatmaps and scatter plots are generated to display the distribution

of the localized monoclinic lattice parameters ( $a$ ,  $b$ ,  $c$ ,  $\beta$ ) and total unit-cell volume ( $V$ ), allowing for direct visual comparison with elemental intensity maps (e.g., Ca, Fe, Ti, Cr) and calculated compositional ratios.

The workflow integrates an optional clustering to delineate distinct intracrystalline domains (such as core and discrete rim zones). It includes a Gaussian Mixture Model (GMM; Pedregosa et al., 2011) with a full covariance matrix applied to the combined  $\mu$ -XRD and  $\mu$ -XRF dataset. Unlike spherical or diagonal constraints, the full covariance structure accurately captures anisotropic, correlated distributions and multi-dimensional covariance among lattice distortions and elemental substitutions. Following GMM classification, principal component analysis (PCA) is performed on the clustered dataset to evaluate eigenvalues, cumulative variance ratios, and directional eigenvector loadings for both structural metrics and minor/trace elements.

Finally, a master multivariate dataset, including exact pixel coordinates, GMM clusters, the local lattice parameters, elemental intensities, specific subset of active diffraction peaks, and parameters used in the processing, is aggregated and exported to a comprehensive workbook.

### **3. Results**

#### **3.1. Chemical variations in experimental clinopyroxene**

Across the entire dataset, the studied clinopyroxene grains exhibit a strictly augitic composition (App.1), characterized by endmember proportions ranging between wollastonite ( $Wo_{20-44}$ ), enstatite ( $En_{36-60}$ ), and ferrosilite ( $Fs_{5-20}$ ; Fig. A2).

In sample PU354 (0.001 kbar; Fig. 5), clinopyroxene composition shows moderate variations, displaying narrow changes with interquartile ranges (difference between 75th percentile and 25th percentile; IQRs) between 1.804-1.827 a.f.u. Si,

0.892-0.952 a.f.u. total Mg, 0.793-0.820 a.f.u. Ca. For Na and Ti, IQR compositions yield 0.018-0.019 and 0.003-0.004 a.f.u., respectively. Core and rim textures are relatively homogeneous with differences of < 0.01 a.f.u. for all major elements and < 0.001 a.f.u. for Na and Ti (App. 1).

Sample PU189 (7.5 kbar; Fig. 5) is characterized by clinopyroxene with highly variable interquartile ranges (IQR) in major and minor elements. Specifically, the IQR reaches 1.841-1.926 a.f.u. for Si, 0.645-0.821 a.f.u. for Ca, 0.882-1.068 a.f.u. for Mg, and, with notable variations also seen in total Al (IQR= 0.115-0.221 a.f.u.) and Ti (IQR= 0.006-0.018 a.f.u.). Note that the provided dataset does not differentiate PU189 into core and rim textures because of the complex textures observed on the EPMA map (Fig. 5).

Clinopyroxenes in sample PU178 (10 kbar; Fig. 5) exhibit significant compositional spread, particularly for total Al (IQR= 0.181-0.292 a.f.u.), Ca (IQR= 0.645-0.738 a.f.u.), Mg (0.898-1.017 a.f.u.), and Si (1.830-1.885 a.f.u.). Minor elements are more restricted with IQRs ranging between 0.007-0.013 a.f.u. Ti, and 0.019-0.023 a.f.u. Na. Similar to the PU189 sample, no distinct core-rim textural subdivisions are reported because of the complex chemical zoning.

In sample PU143 (15 kbar; Figs. 2 and 5), clinopyroxene shows extremely variable IQRs for major (1.674-1.873 a.f.u. for Si, 0.790-0.983 a.f.u. for Mg, 0.543-0.720 a.f.u. for Ca, 0.216-0.613 a.f.u. for Al) and minor elements (0.006-0.032 a.f.u. for Ti, 0.025-0.031 a.f.u. for Na). The transition from core to rim textures is marked by a significant depletion in Si, Mg, and Ca, coupled with a strong enrichment in Al, Fe, Ti, and Na (Fig. 2; App. 2).

In sample PU158 (35 kbar; Fig. 5), clinopyroxene composition is relatively homogeneous in core and rim, with little compositional variations for major elements

413 (IQR= 1.951-1.959 a.f.u. for Si, 0.138-0.160 a.f.u. for Al) and high Na contents (0.072-  
414 0.089 a.f.u. Na).

### 415 **3.2. Single-crystal XRD measurements**

416 Single-crystal X-ray diffraction confirms that all three analyzed clinopyroxene  
417 samples (PU189, PU158, and PU178; App. 2) crystallize in the monoclinic system,  
418 assigned to the C2/c space group setting. The structure refinements yielded reliable  
419 final  $R_1$  indices ( $I > 2\sigma(I)$ ) of 0.0957 for PU189, 0.0386 for PU158, and 0.0408 for  
420 PU178, with goodness-of-fit values ranging tightly between 1.076 and 1.409. Unit-cell  
421 volumes exhibit variations between the charges, with sample PU189 displaying the  
422 most expanded lattice at 436.52 Å<sup>3</sup>, compared to 434.37 Å<sup>3</sup> for PU158 and 434.84 Å<sup>3</sup>  
423 for PU178. The transformed C2/c lattice parameters reveal corresponding beta angles  
424 that remain consistently bounded between 106.54° and 106.61°.

425 Refinement of the atomic site occupancies and polyhedral volumes further  
426 characterizes the structural variations. The M2 (CN8) sites, which accommodate Ca  
427 occupancies ranging from 0.744 to 0.839 and Mg occupancies from 0.161 to 0.256,  
428 maintain polyhedral volumes between 27.465 Å<sup>3</sup>, and 27.641 Å<sup>3</sup>. The M1 (CN6)  
429 octahedral sites present volumes from 11.679 Å<sup>3</sup> to 11.772 Å<sup>3</sup> and are strongly  
430 dominated by Mg (0.89–0.959), with minor Fe incorporation (0.041–0.11). In contrast,  
431 the tetrahedral SiO<sub>4</sub> (CN4) volumes remain highly conserved across the samples,  
432 showing a minimal spread from 2.228 Å<sup>3</sup> to 2.249 Å<sup>3</sup>.

### 433 **3.3. Spatial distribution of lattice parameters**

434 Two samples have been investigated with synchrotron-based XRD mapping:  
435 PU143 crystallized at 15 kbar (1200 °C) and PU354 formed at 0.001 kbar (1175 °C).

These samples were primarily selected for their contrasting formation pressures but relatively similar formation temperatures, alongside their distinct chemical compositions and zoning patterns (Figs. 2, 5, and 6).

In sample PU143 (15 kbars, Fig. 6A),  $\mu$ -XRD measurements performed at a step of measurement of 1.5  $\mu\text{m}$  on clinopyroxene show pronounced spatial zoning in lattice parameters. In order to segment distinct domains within the crystal grains, a Gaussian mixture model (GMM) using a full covariance matrix was applied to the combined multi-dimensional space of coupled s- $\mu$ XRD lattice metrics (a, b, c, beta-angle, cell V) and  $\mu$ -XRF elemental intensities (Ca, Fe, Ti, Cr). This probabilistic approach successfully resolved three distinct compositional-structural clusters (cluster 1–Core, cluster 2–Rim, and cluster 3–mixture Rim-core; Fig. 7). The mixed core-and-rim composition of cluster 3 is confirmed by lower Ca and Cr intensities in the  $\mu$ -XRF maps. This feature is invisible in BSE and EPMA data because those techniques are highly surface-sensitive (penetrating only a few  $\mu\text{m}$ ), whereas X-rays interact with a larger volume and probably the full  $\sim 30\text{ }\mu\text{m}$  sample thickness during  $\mu$ -XRF mapping (Flude et al., 2017). In the core domains (cluster 1,  $n=204$ ), a limited lattice parameters variation is observed, yielding a mean unit-cell volume of  $434.55\text{ }\text{\AA}^3$  (IQR of  $433.45\text{--}435.32\text{ }\text{\AA}^3$ ) and a mean beta angle of  $106.19^\circ$  (IQR of  $105.93\text{--}106.40^\circ$ ). Spatially, the core domain is characterized by larger a and b lattice parameters but a noticeably smaller c parameter and beta angle relative to the rim domains. The rim domains (including clusters 2 & 3, total  $n=132$ ) display significantly wider dispersion across all crystallographic parameters (Fig. 7A). The rim domains feature a broader unit-cell volume spread (IQR of  $432.88\text{--}436.78\text{ }\text{\AA}^3$ ) and higher beta angles (IQR of  $106.43\text{--}106.73^\circ$ ). Principal component analysis (PCA) performed post-clustering highlights that the primary axes of variance (PC1 and PC2) effectively separate core (cluster 1)

and rim clusters (cluster 2 and 3) along specific elemental substitution vectors (Ca-Cr enrichment versus Fe-Ti) coupled with higher beta angle in the rim clusters (Fig. 7B, C).

Furthermore, analysis across a continuous core-rim transect in sample PU143 confirms this intra-crystalline structural heterogeneity (step of measurement = 0.3  $\mu\text{m}$ ; Fig. 2). Lattice parameters differences are observed between core-rim textures with a core showing lower beta angles compared to the rim, with mean beta angles of 105.8° (IQR of 105.7-106.1°) and 106.8° (IQR of 106.7-106.9°), respectively (Fig. 8C).

Sample PU354 (0.001 kbar; Fig. 6B) includes clinopyroxene intergrown with spinel, which required strict spatial segmentation to eliminate sub-surface artifacts from the adjacent phase. Unlike zoned samples (i.e., PU143), these crystals lack significant core-rim textures (Fig. 5) and maintain spatially homogeneous lattice parameters. For the primary measured grain group ( $n=235$ ), the mean unit-cell volume is large, yielding 443.69  $\text{\AA}^3$  (IQR of 443.31-444.28  $\text{\AA}^3$ ), driven by expanded mean  $b$  (8.98  $\text{\AA}$ ), and  $c$  (5.29  $\text{\AA}$ ) axes. However, inversely to its expanded volume, PU354 exhibits a low  $\beta$  angle, averaging 105.38° (IQR of 105.24°-105.53°; Fig. 8A). A secondary group of measurements taken across multiple grains in sample PU354 ( $n=63$ ) yields a similarly expanded mean unit-cell volume of 443.71  $\text{\AA}^3$  (IQR of 443.27-444.34  $\text{\AA}^3$ ). This overall volume is maintained through a slightly longer mean  $a$  axis (9.71  $\text{\AA}$ ) and a correspondingly shorter  $b$  axis (8.94  $\text{\AA}$ ) compared to the primary grains, while the  $c$  axis remains consistent at 5.29  $\text{\AA}$ . Notably, this secondary grain group exhibits an even lower  $\beta$  angle, averaging exactly 105.00° (IQR between 104.86° and 105.10°; Fig. 8A-C).

#### 4. Discussion and implications

#### 4.1. Evaluating s- $\mu$ XRD for microscale lattice parameter mapping

The successful application of s- $\mu$ XRD for microscale crystallographic mapping relies heavily on the initial chemico-spatial deconvolution. In complex, multiphase geological materials, particularly in standard 30- $\mu$ m-thick sections where the transmitted X-ray beam may interact with overlapping crystals, a robust chemical mask is critical. By applying stringent compositional thresholds (such as Ca intensity and Ca/Fe ratios; Fig. 2) derived from simultaneous  $\mu$ XRF or prior EPMA mapping, the workflow actively decouples the clinopyroxene diffraction signal from the surrounding groundmass and co-crystallizing phases like olivine. This targeted spatial isolation minimizes the potential overlap of diffractions peaks in reciprocal space, drastically reducing indexing ambiguities and ensuring that background scatter is not falsely mathematically fitted during the refinement loop.

A major methodological advantage of this processing pipeline is its dynamic approach to baseline lattice calibration. Initially, the reference unit-cell is estimated using the compositional equations of Morrison et al., (2018); however, this purely chemical derivation serves only as a first-order approximation. Relying strictly on composition-based estimates risks systematic misindexing, particularly in zoned crystals subjected to localized thermo-mechanical strain. To overcome this limitation, the current workflow actively adapts to the empirical diffraction data. By performing a global pre-refinement against the most robust experimental reflections, the algorithm overwrites the theoretical baseline with an optimized, sample-specific reference cell. This ensures the subsequent localized mapping is anchored to crystallographic measurements rather than compositional proxies.

Ultimately, this study demonstrates that s- $\mu$ XRD provides highly accurate, spatially resolved estimates of clinopyroxene unit-cell parameters that align well with

established bulk data for similar clinopyroxene (Fig. 9A-B). Quantifying these subtle crystal structure variations at the microscale allows the technique to successfully bridge traditional single-crystal analysis and high-resolution chemical mapping. As this methodology is expanded to encompass a broader array of experimental charges and compositionally complex natural clinopyroxenes, the ability to directly map in-situ lattice distortions has the potential to improve our understanding of magmatic systems, providing unprecedented insights into magma plumbing architecture, storage conditions, and transient kinetic processes (Nazzareni et al., 2021; Tommasini et al., 2022).

#### **4.2. s- $\mu$ XRD vs. SC-XRD: Methodological constraints across sample types**

Conventional single-crystal X-ray diffraction (SC-XRD) remains the gold standard for absolute structural refinement on single crystals, especially on clinopyroxene where 10's of studies have employed SC-XRD to estimate formation pressure of magmas (Dal Negro et al., 1989; Nimis, 1995; Tommasini et al., 2022). SC-XRD measurements physically integrate the diffraction signal across the entire volume of an isolated, extracted grain ( $> 50 \mu\text{m}$ ) and act as a bulk-averaging technique. Then, its application to complex and zoned geological materials is fundamentally limited by a lack of spatial resolution (typically above 50-100  $\mu\text{m}$ ; Grey, 2022). If a clinopyroxene crystal exhibits significant internal chemical zoning, a ubiquitous feature in both experimental charges and natural magmatic systems (Dal Negro et al., 1986; MacDonald et al., 2024; Schoneveld et al., 2020), SC-XRD inevitably produces a homogenized, average unit-cell that hides localized chemically-related structural variations. While this "bulk" approach may be suitable for perfectly

equilibrated, unzoned crystals, it proves inadequate for extracting high-resolution temporal records from dynamic magmatic environments (Tommasini et al., 2022).

A compilation of single-crystal XRD (SC-XRD) data for natural magmatic clinopyroxenes, spanning from deep mantle xenoliths (Cameron and Papike, 1981; Chelazzi et al., 2006; Dal Negro et al., 1989, 1982; Secco et al., 1995) to shallower calc-alkaline and alkaline systems (i.e.; Aydin et al., 2009; Dal Negro et al., 1985; Nazzareni et al., 2003, 1998; Pasqual et al., 1995; Pasquale and Francesco, 1998), demonstrates a broad correlation between unit-cell volume,  $\beta$  angle, and formation pressure (Negro et al., 1984). However, a precise quantitative calibration linking formation pressure to lattice parameters for experimental clinopyroxenes is currently lacking. The correlation between lattice parameters variations and formation pressure has only been empirically modelled by the barometer of Nimis (1999).

Our SC-XRD analyses of both unzoned (PU158) and intensely zoned experimental crystals (PU178 and PU189; Fig. 5) highlight a critical methodological limitation in establishing correlation between lattice parameters and formation pressure using SC-XRD measurements. Sample PU158, which crystallized at 35 kbar, produced compositionally uniform crystals. The crystallographic data from this sample aligns perfectly with established SC-XRD literature for mantle xenoliths crystallized at high-pressure (Chelazzi et al., 2006; Dal Negro et al., 1989), confirming that SC-XRD yields reliable unit-cell parameters and  $\beta$  angles for unzoned clinopyroxene. In contrast, the clinopyroxenes from samples PU189 (7.5 kbar) and PU178 (10 kbar) exhibit pronounced chemical zoning (Fig. 5) and yield structurally questionable lattice parameters values (Fig. 9A). Notably, the SC-XRD refinements for PU189 (7.5 kbar) and PU178 (10 kbar) plot within the mantle xenolith field, exhibiting unit-cell and similar  $\beta$ -angle parameters comparable to those of PU158 (35 kbar), contradicting the

expected pressure-unit-cell volume relationship (Fig. 9A). We suggest that intense chemical zoning fundamentally precludes the use of bulk SC-XRD for accurate lattice parameter estimation. Furthermore, the data quality and the presence of a mixture of atoms with similar scattering power (for atoms adjacent in the periodic table) do not allow us a reliable refinement of the chemical composition. It prevents a precise correlation of the unit-cell parameters with the chemical composition and with temperature and pressure. Experimental and natural magmatic clinopyroxenes are characteristically zoned (e.g., sector and oscillatory zoned; Marxer et al., 2022; Métrich and Rutherford, 1998; Sisson and Grove, 1993; Ubide et al., 2019; Ulmer et al., 2018), attempting to capture their crystal structure via bulk SC-XRD inherently averages discrete growth domains. Additionally, SC-XRD analyses revealed that none of the crystals were true single crystals: most of them showed polydomain of clinopyroxene (with a maximum fraction of only 30% of reflections belonging to one domain) or even polycrystals with a mixture of other mineral phases (orthopyroxene, olivine, etc...). These microstructural characteristics significantly limit the accuracy of unit-cell parameter measurements and structural refinements. As shown in Figure 8A-B, existing literature with SC-XRD measurements often suffers from broad uncertainties, making it difficult to distinguish between magma crystallized at various pressure. Although mantle xenoliths and sub-alkaline series generally display smaller unit-cell volumes and higher beta angles (Fig. 9), the reliance on bulk-averaged data systematically misrepresents true localized lattice parameters in dynamic magmatic environments with zoned clinopyroxenes.

In contrast, the spatially resolved nature of s- $\mu$ XRD successfully overcomes this critical analytical limitation. As demonstrated in Figs. 7 and 8, s- $\mu$ XRD is capable of explicitly differentiating core and rim domains within individual zoned crystals. For

instance, the synchrotron data for sample PU143 clearly resolves distinct cell volumes and  $\beta$  angles for the core (yellow circle) versus the rim (grey circle). The crystal structure signature captured by s- $\mu$ XRD directly tracks the pronounced chemical zoning observed in the corresponding EPMA maps, where core and rim domains exhibit drastic compositional variations in major elements, with the wollastonite and jadeite end-members varying by a factor  $\sim 1.5$ -2 between the two textures (Fig. 9C).

The ability to mathematically and spatially decouple core and rim lattice parameters carries profound implications for petrological modelling. Because crystal structures respond directly to evolving intensive variables (pressure, temperature) and fluctuating melt compositions, chemical zoning drastically influences lattice parameters (Tommasini et al., 2022). If a strongly zoned clinopyroxene is analyzed solely via one SC-XRD measurement, the resulting "bulk" lattice volume does not represent a true, discrete thermodynamic state, but rather an addition of multiple, distinct growth stages. By preserving the exact spatial context of these localized structural domains, s- $\mu$ XRD ensures that subsequent thermobarometric calculations are anchored to specific compositional zones, thereby preventing erroneous and averaged pressure-temperature conditions.

#### **4.3. Implications for clinopyroxene thermobarometry and other mineral systems**

The integration of in-situ s-XRD mapping to measure experimental and natural geological samples may improve significantly the resolution and accuracy of clinopyroxene barometry in dynamic magmatic systems. Traditional thermobarometric models for volcanic systems rely on chemical spot analyses compositions within clinopyroxene and those of the coexisting melt (Neave and Putirka, 2017; Putirka,

2008) to indirectly infer crystallization pressures via empirically-calibrated thermodynamic equations. S- $\mu$ XRD mitigates the uncertainties of indirect chemical proxies by providing direct, high-resolution measurements (few  $\mu\text{m}$  in spatial resolution) of the crystal lattice in both experimental and natural materials. In rapidly ascending mafic systems, extreme pressure-temperature gradients frequently generate sharply zoned phenocrysts (Ubide et al., 2019). Extracting the absolute, localized unit-cell volume ( $V$ ) in the primitive core through high-resolution mapping may enable a far more precise determination of crystallization depths. Consequently, this approach mitigates the risk of homogenizing crystallographic parameters across discrete magmatic pulses, ensuring that calculated thermodynamic conditions accurately reflect distinct stages of crustal storage and magma transport.

The utility of this spatially resolved crystallographic technique extends significantly beyond clinopyroxene. Future application of in-situ XRD mapping to other ubiquitous magmatic phases, such as olivine, amphibole, and plagioclase, will be essential for developing a more holistic, multi-mineral approach to crystallographic thermobarometry. Because different mineral lattices respond uniquely to specific intensive variables (pressure, temperature), simultaneously mapping crystal structure distortions across multiple co-crystallizing phases within a single thin section could yield independent, cross-validated P-T estimates. This multimodal approach would be particularly valuable for deciphering complex open-system processes, such as magma mixing or crustal assimilation (Grondahl and Zajacz, 2017; Ubide et al., 2019), where distinct mineral populations within the same volcanic rock record completely divergent thermodynamic and kinematic histories prior to eruption.

Beyond fundamental volcanology, the ability to resolve microscale crystal structure constraints holds significant potential for economic geology, particularly in evaluating

orthomagmatic ore deposits hosted within mafic-ultramafic intrusions (Ni-Cu-platinum group element; Barnes et al., 2020; Eales and Costin, 2012; Schoneveld et al., 2020). In these mineralized systems, clinopyroxene frequently crystallizes alongside or physically entraps critical base and precious metal sulfides. Coupling localized  $\mu$ XRD lattice parameters with quantitative trace element partitioning data can help pinpoint the precise physicochemical triggers, such as abrupt depressurization events or crystal structure re-equilibration, that drive sulfide liquid immiscibility and metal accumulation. By mapping these coupled crystal structure and chemical relationships in magmatic minerals in-situ, researchers can better constrain the highly localized intensive parameters governing ore precipitation, ultimately refining the genetic models and exploration vectors for deeply rooted magmatic plumbing systems.

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## 7. Table caption

Table 1. Summary of experimental run conditions, applied XRD techniques (synchrotron-based s-μXRD vs. single-crystal XRD), starting materials, phase assemblages, corresponding compositional proportions, and experimental pressures and temperatures.

## 8. Figure captions

Figure 1. Schematic comparison of X-ray diffraction (XRD) techniques for mineral characterization. (A) Standard single-crystal XRD (SC-XRD) operates in angle-dispersive mode. A fixed-energy monochromatic X-ray beam (fixed  $\lambda$ ) irradiates a relatively large, isolated crystal fragment (>50 μm). The sample is physically rotated (changing  $\theta$ ) to satisfy Bragg's law and project a 3D diffraction pattern onto the detector. (B) Synchrotron-based micro-XRD (s-μXRD) using an energy-dispersive mapping approach. The thin lamellae sample originating from standard 30 μm thin section remains completely stationary (fixed  $\theta$ ) while the incident X-ray beam is tuned across a continuous energy spectrum (changing  $\lambda$ , e.g., 13.0 to 21.0 keV). This

configuration enables in-situ spatial mapping of lattice parameters across micro-domains and integrates an X-ray fluorescence (XRF) detector for simultaneous, coupled chemical characterization.

Figure 2. Chemical spatial deconvolution of zoned clinopyroxene (sample PU143, crystallized at 15 kbar). (Left) EPMA backscattered electron (BSE) image, phase classification (discriminating clinopyroxene core and rim textures), and Ca and Na intensity maps. The red box on the BSE image indicates the synchrotron  $\mu$ -XRF scan area. (Right) Synchrotron  $\mu$ -XRF intensity maps (Ca, Cr, Ti) and the subsequent chemical masking workflow in the ROI. A transect of  $\mu$ -XRD analyses is located with a red dashed line zone. Compositional thresholds (normalized Ca > 0.4 and Cr > 0.4) are applied to generate a final binary mask (bottom right), effectively isolating the clinopyroxene diffraction signal from the surrounding matrix for further s- $\mu$ XRD processing.

Figure 3. Workflow for s- $\mu$ XRD data processing and 3D reciprocal space reconstruction. (A) Raw detected reflections mapped at 20.8 keV. (B) Spatial intensity distribution at 20.8 keV of a single isolated reflection (located in red in (A)). (C) Automated vectorization and "blob" detection of diffraction peaks at 20.8 keV using enhanced normalized intensity. (D) Stacking and position interpolation of XRD maps acquired across a multi-energy sweep (e.g., 20.8 down to 14 keV). (E) Final 3D reciprocal space visualization (qx, qy, qz) generated from the stacked energy maps and visualized in two ways, displaying the fully integrated reflections across all spatial positions. The total amount of "raw" reflections yields over 230,000.

Figure 4. Density-based spatial clustering (DBSCAN) in reciprocal space and reflection indexing validation. (A) 3D reciprocal-space point clouds displaying intensity-scaled reflection clusters alongside rejected background spots (in grey). (B) Correlation between experimental and theoretical d-spacings across indexed lattice planes, color-coded by relative d-spacing mismatch on a log-scale. (C) Filtering criteria for crystal refinement, showing indexing residual versus spot count per reflection with thresholds applied (minimum 100 spots and maximum residual  $>0.02$  Å). The inset illustrates localized d-spacing variations mapped across the crystal domain in the ROI.

Figure 5. EPMA phase maps and corresponding elemental distribution maps (Ca, Cr, Na) for experimental charges synthesized across a range of pressures: PU354 (0.001 kbar), PU189 (7.5 kbar), PU178 (10 kbar), and PU158 (35 kbar). The phase distributions highlight variations in co-crystallizing assemblages (including clinopyroxene, olivine, plagioclase, amphibole, orthopyroxene, garnet, glass, and spinel). Intensity maps are segmented to see only clinopyroxene in the map. It shows the intra-crystalline zoning, and distinguishes between weakly zoned clinopyroxenes in our low- and high-pressure runs (PU354, PU158) and heavily zoned, chemically heterogeneous grains in our intermediate-pressure charges (PU189, PU178).

Figure 6. Synchrotron  $\mu$ -XRD spatial maps of unit-cell parameters (a, b, c),  $\beta$  angles, unit-cell volumes, and refinement R-factors. (A) Clinopyroxene grain from sample PU143 (15 kbar, 1200 °C) with intra-crystalline structural zoning. (B) Clinopyroxene grain from sample PU354 (0.001 kbar, 1200 °C), showing a restricted region of interest to limit subsurface spinel interference on the XRD signal.

Figure 7. Multivariate spatial clustering, principal component analysis (PCA), and variance distribution applied to the combined X-ray diffraction (XRD) and X-ray fluorescence (XRF) dataset. (A) Spatial distribution map using gaussian mixture model clustering: across pixel coordinates identifying three distinct structural-compositional domains: Cluster 1 (core, medium green), Cluster 2 (Rim, dark green), and Cluster 3 (mixture rim-core, light green). (B) Principal component analysis (PCA) applied after clustering with PCA1 versus PCA2 illustrating multivariate cluster separation, overlaid with loading vectors for crystallographic unit-cell parameters (a, b, c, and beta angle) and characteristic elemental intensities (Ca, Cr, Fe, Ti). (C) Plot showing eigenvalues (black solid curve with markers, left axis) and cumulative explained variance ratio (red dashed curve, right axis) as a function of principal components, highlighting the efficiency of dimensionality reduction for the dataset.

Figure 8. Statistical distributions and cross-comparisons of clinopyroxene lattice parameters (a, b, c),  $\beta$  angles, and unit-cell volumes across experimental charges. (A) Box plots illustrating spatial variations across different analytical domains, including whole grains, rims, cores, and core-rim transect for samples PU354 and PU143. (B, C) Plots comparing unit-cell volume versus b parameter (B) and  $\beta$  angle (C) for  $\mu$ XRD spatial zones against conventional single-crystal XRD (SC-XRD) measurements for weakly zoned (PU158) and heavily zoned (PU178, PU189) experimental charges.

Figure 9. Comparative analysis of experimental clinopyroxene structural data against global single-crystal XRD literature datasets. (A)  $\beta$  angle versus unit-cell volume and (B) volume expansion index  $[\text{Wo}+\text{Fe})-(\text{Jd}+\text{Aeg})]$  versus unit-cell volume, contrasting

903 s- $\mu$ XRD and SC-XRD experimental charges with natural literature compilations  
904 categorized by magma type and jadeite content. (C) EPMA-derived Wollastonite (Ca)  
905 and Jadeite (Na) end-member (Neave et al., 2024) weight percentages for core and  
906 rim domains across all experimental samples, showing difference in zoning between  
907 the experimental charges studied.  
908

| #     | XRD technique     | Starting material | Composition (%)                                                                                                                     | Pres. (Kbar) | Temp. (°C) |
|-------|-------------------|-------------------|-------------------------------------------------------------------------------------------------------------------------------------|--------------|------------|
| PU354 | Synchrotron-based | Picrobasalt       | <b>cpx</b> , L, ol, plag, sp<br><b>3.4(3)</b> , 65.2(13), 17.5(5),<br>10.4(8), 3.5(10)                                              | 0.001        | 1175       |
| PU143 | Synchrotron-based | Picrobasalt       | <b>cpx</b> , L, ol<br><b>10.8(7)</b> , 75.1(7), 14.2(3)                                                                             | 15           | 1200       |
| PU189 | Single-crystal    | Picrobasalt       | <b>cpx</b> , L, ol, opx, plag,<br>amph, ilm, sp<br><b>19.6(31)</b> , 3.6(34), 10.0(60),<br>25.7(75), 20.0(39), 20.8(108),<br>0.3(5) | 7.5          | 1000       |
| PU178 | Single-crystal    | Picrobasalt       | <b>cpx</b> , opx, plag,<br>amph, sp, ilm<br><b>15.9(34)</b> , 28.2(30), 13.1(22),<br>42.4(76), 0.4(9)                               | 10           | 1000       |
| PU158 | Single-crystal    | Picrobasalt       | <b>cpx</b> , L, opx, gar<br><b>44.3(14)</b> , 10.1(13), 0.8(12),<br>44.8(14)                                                        | 35           | 1200       |

Table 1

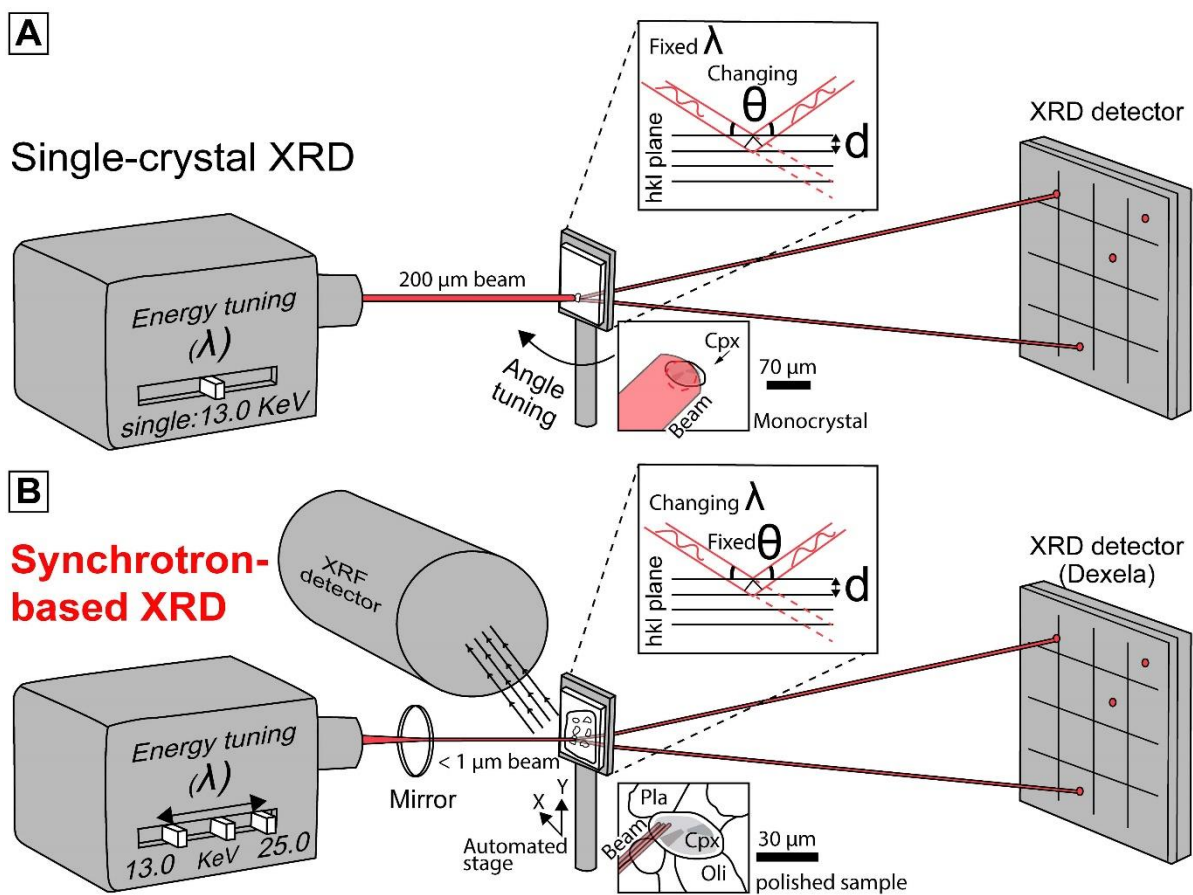


Figure 1

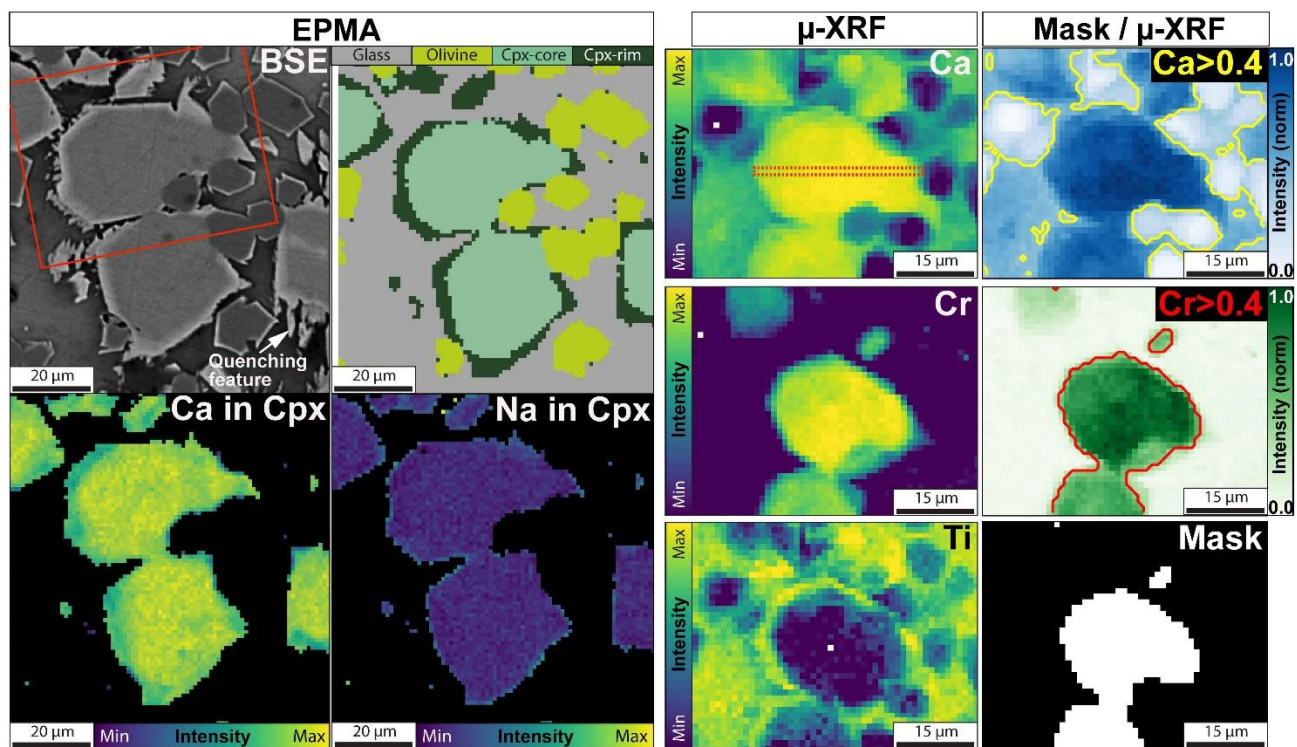
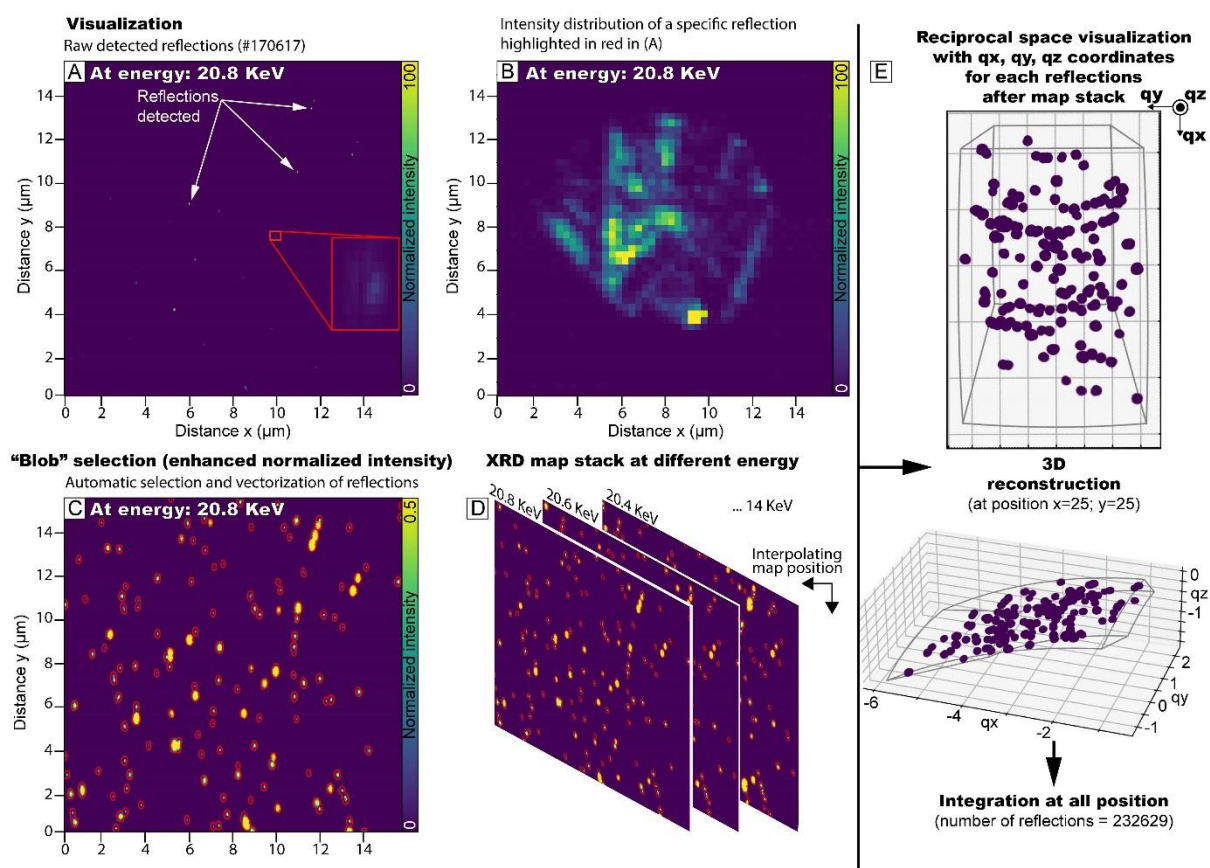


Figure 2



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918 Figure 3

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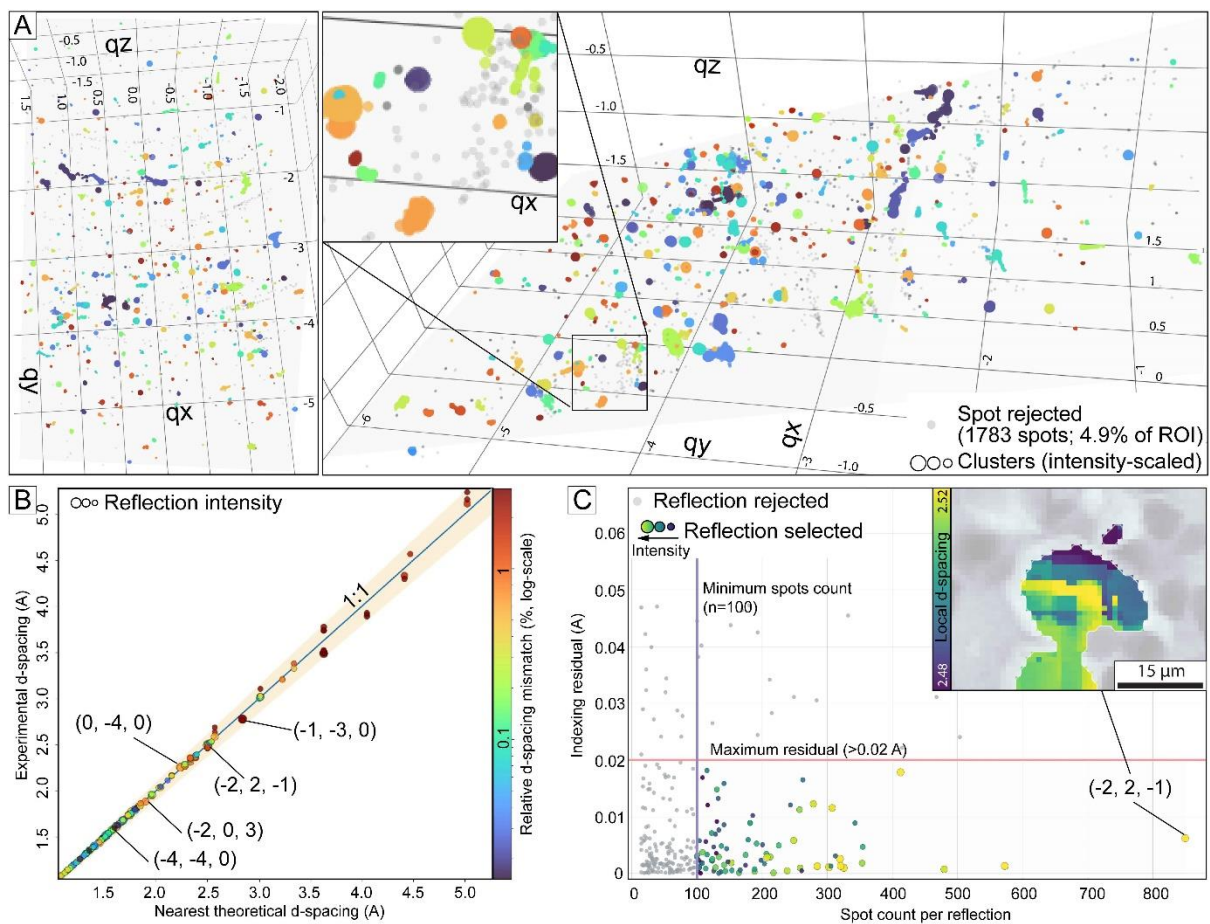


Figure 4

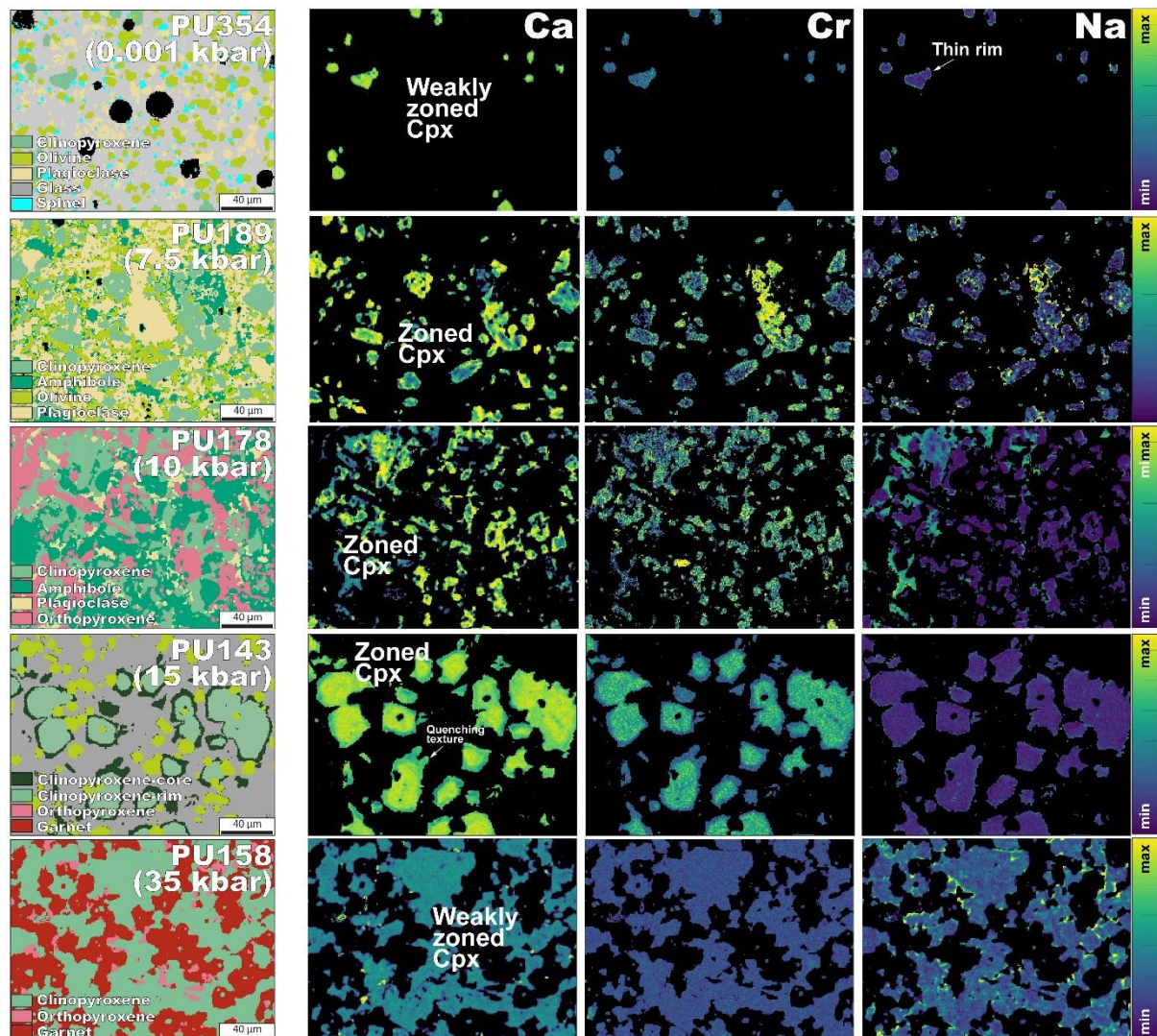


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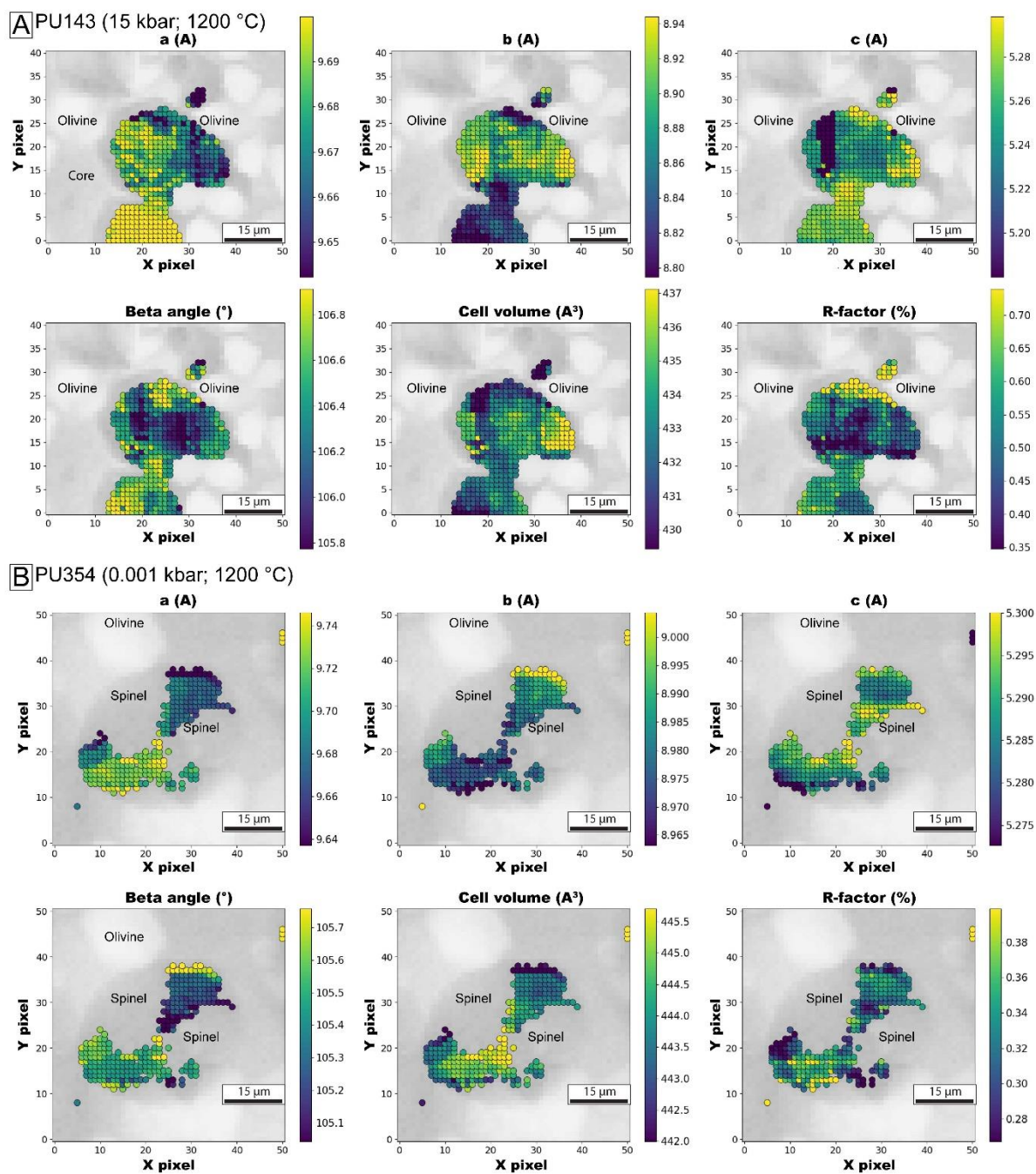


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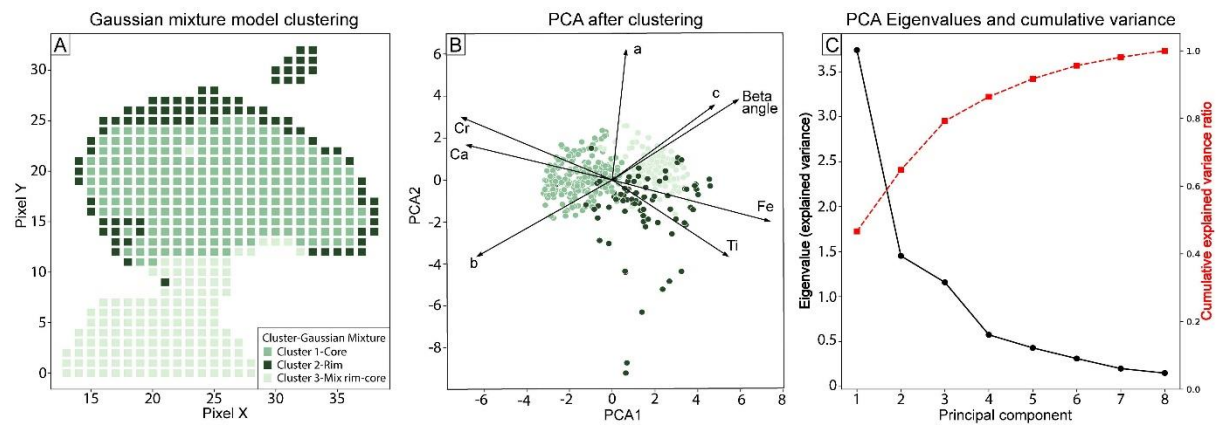


Figure 7

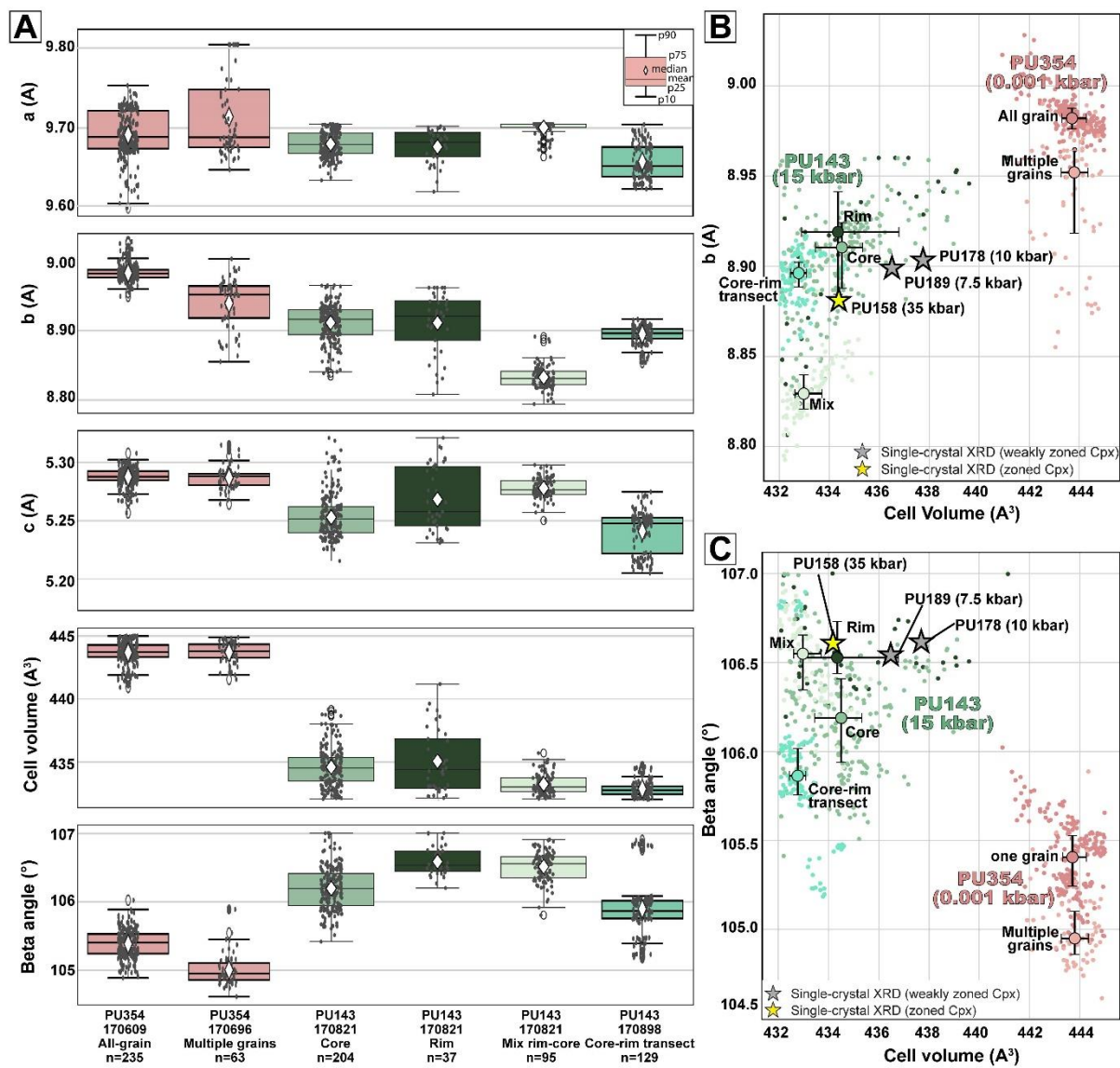
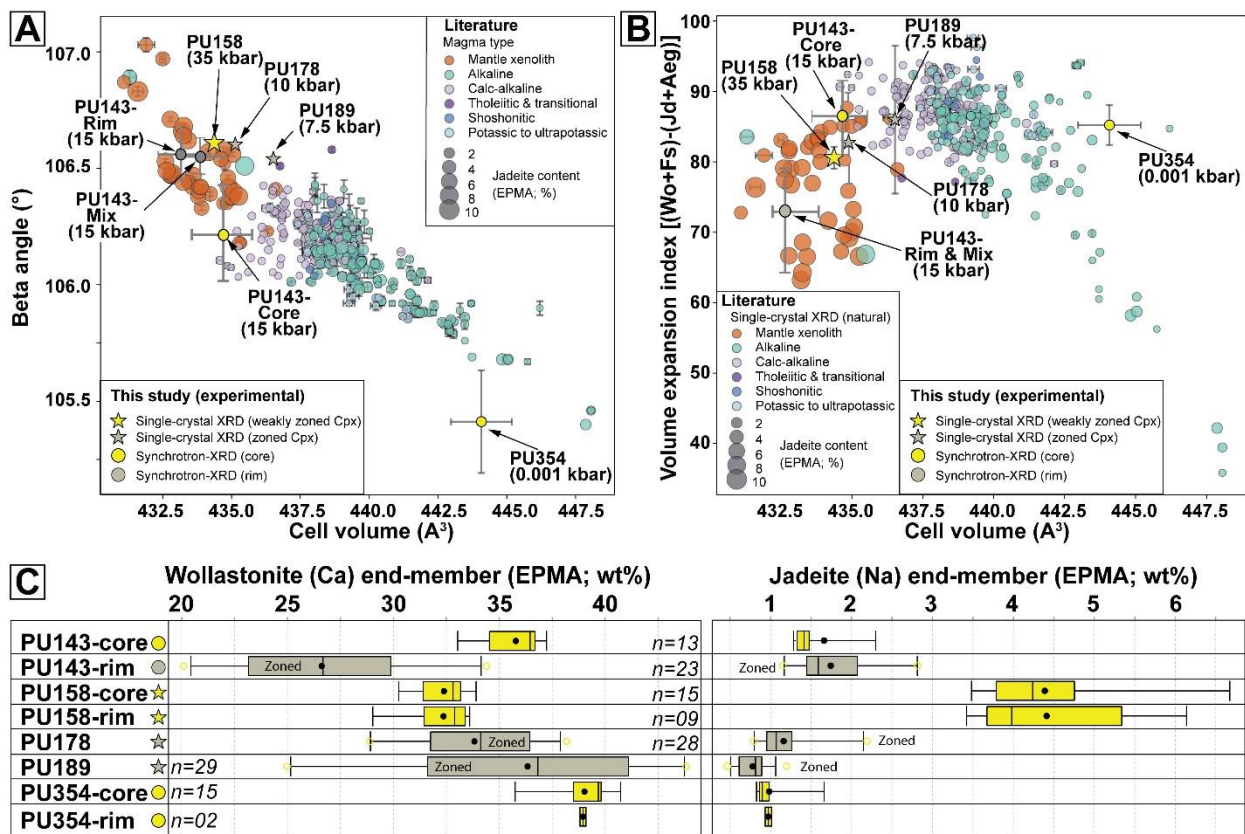


Figure 8



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