Exploring diamond inclusions via combined Microtomography and single-crystal X-ray Diffraction at GSECARS

Stella Chariton, Vitali B. Prakapenka, Mark Rivers, Christofanis Skordas and Dongzhou Zhang

Center for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60637, USA

Introduction to the problem

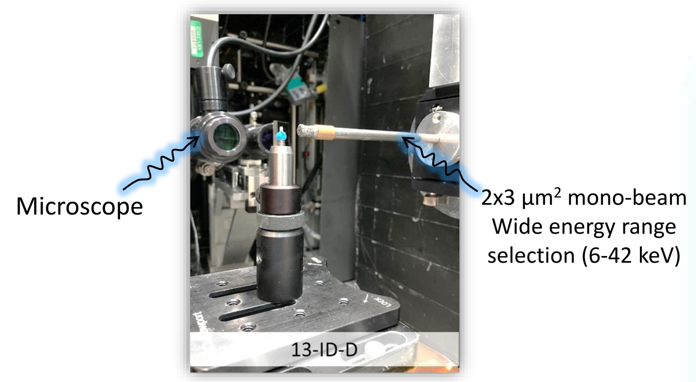
Diamond inclusions represent a direct window into the deepest layers of our planet and although rare specimens, the information they carry is invaluable in determining the mantle chemistry and understanding processes such as mantle composition, convection and volatile cycling.

A suite of techniques may be used to study diamond inclusions and to identify the phases entrapped. However, many are considered destructive, often requiring exposure of the inclusion to the surface by diamond polishing. Such approaches pose a significant risk to the analysis and results interpretation due to possible alteration of the inclusions by exposure to the atmospheric air and pressure as well as loss of fluid phases or volatiles.

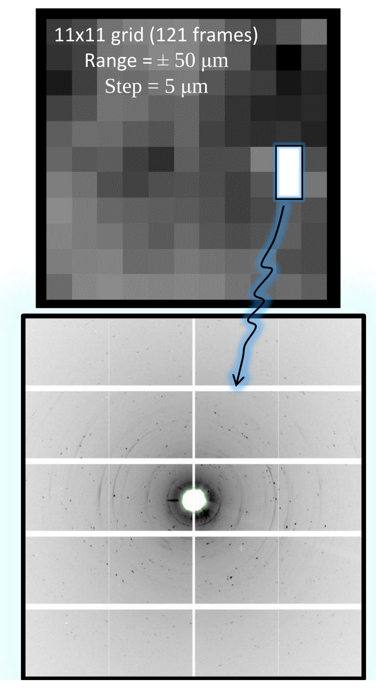
Common Procedures for sub-surface inclusions so far…

1. Mount
2. "Optical" alignment
3. Large XRD maps
4. Hope for the best…

Trivial , Time consuming & not always rewarding



The 13ID-D line at GSECARS is often used to study diamond inclusions and new minerals have been discovered here (Tschauner et al. 2014; 2018). Users particularly benefit from the small beam size and the high flux. However, sub-surface inclusions remain a challenge at this beamline.



The inclusion of interest is 10 µm size big and very hard to locate and center upon

Synchrotron single-crystal X-ray diffraction is a powerful and unique tool in unravelling complex mineral assemblages by allowing accurate structure determination and phase identification. A critical requirement for a successful data collection is to bring the inclusion in the center of rotation axis (Fig 2.) . This is easily done for exposed inclusions using an optical approach (a.k.a. microscope camera). However, studying sub-surface inclusions present a great challenge during alignment procedures. Due to the diamond refraction index or opaque areas, it is very hard to align optically on a non-exposed inclusion (Fig. 1.). A badly centered inclusion escapes the X-ray beam during collections (Fig. 2a.) which results in severely incomplete datasets (Fig. 2b).

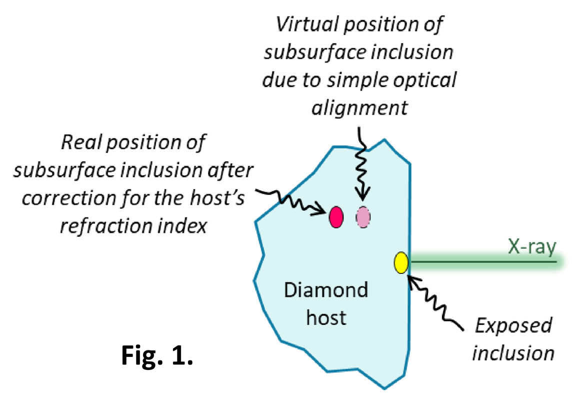


Fig. 1.

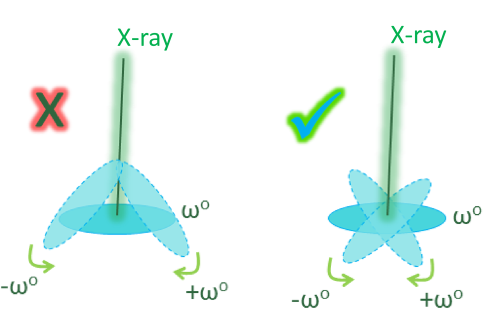


Fig 2a. A crystal must always remain under the X-ray beam during the rotational data collection.

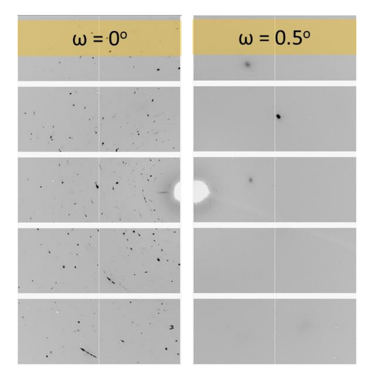


Fig. 2b. Example of a badly centered crystal. Reflections disappear instantly.

How to solve the problem

At the 13BM-D beamline at GSECARS we combined microtomography (CMT) and SCXRD to approach this problem:

1. Scan diamonds with unfocused pink or monochromatic beam to produce a series of high contrast absorption images (Fig. 4.)
2. Filtered back-projection analysis produces their 3D reconstructed images (Fig. 5)
3. This allows the visualization, location and alignment of inclusions with focused X-ray beam to collect SCXRD patterns (Fig. 6)
4. SCXRD data analysis allows accurate phase identification and structure solution and refinements

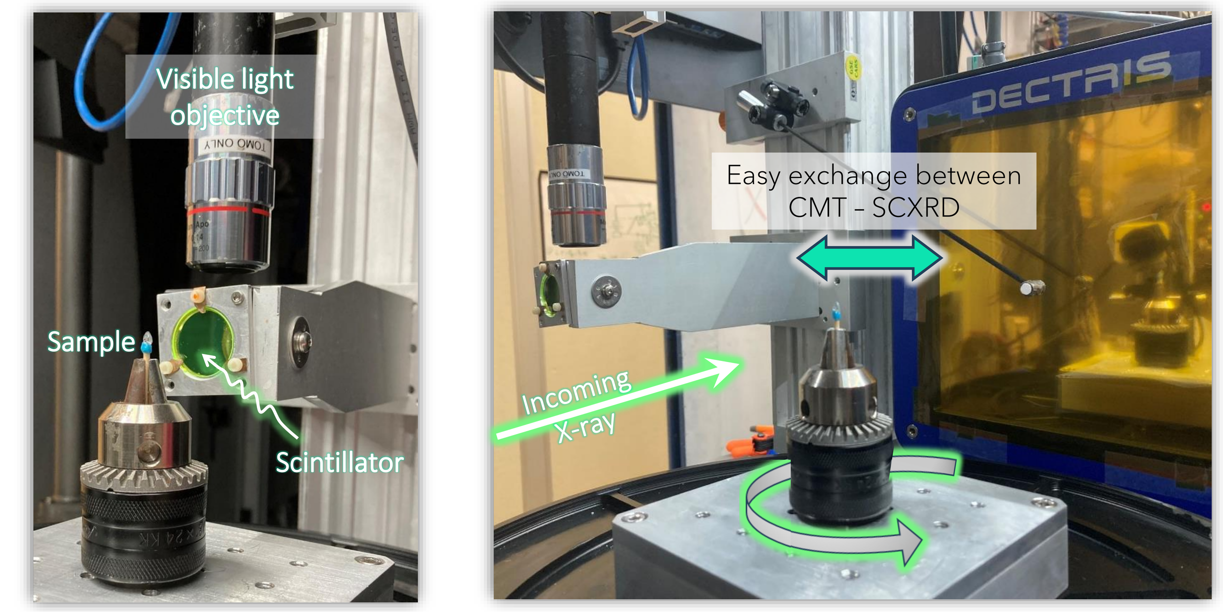


Fig. 3 . *The set-up used to study diamond inclusions at 13BM-D allows swift on-line alternation between the two techniques.*

Ask me for Videos!

Fig. 4 . *Absorption Images*

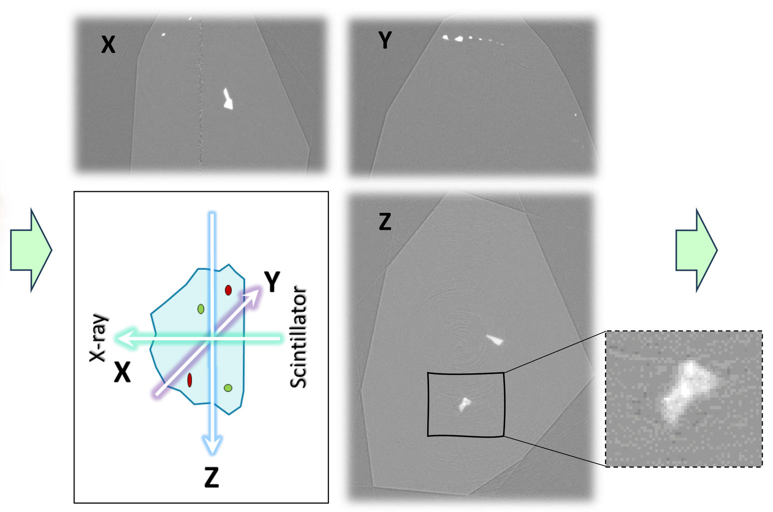


Fig. 5 . *Reconstructed images along X-Y-Z*

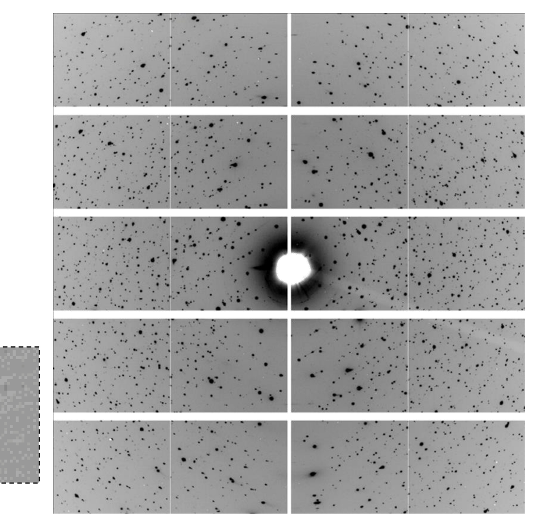


Fig. 6. *SCXRD collected from a multigrain/multiphase inclusion.*

Overview

STEP 1: X-ray Computed Microtomography
Locate, Visualize & Align

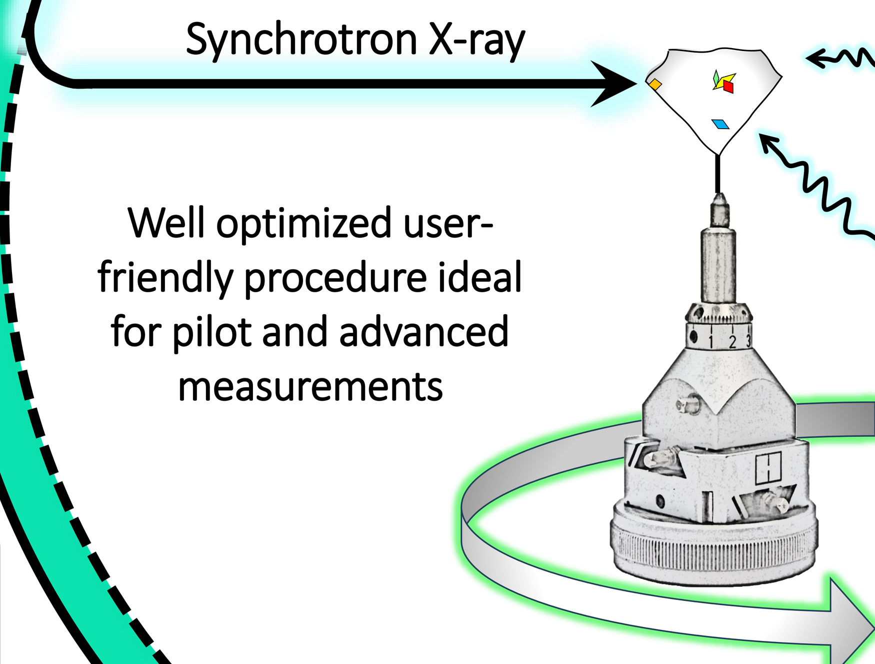
STEP 2: Single-crystal X-ray Diffraction
Identify phases & solve crystal structures

Synchrotron X-ray

Prefer free-standing samples

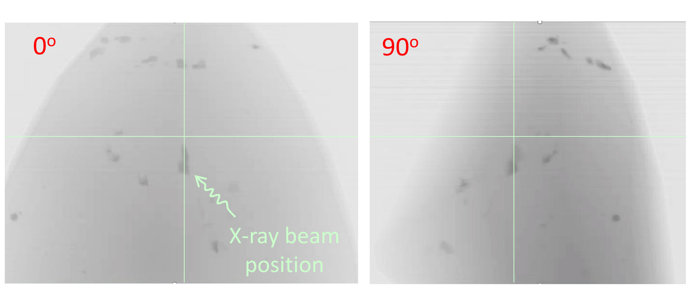
Well optimized user-friendly procedure ideal for pilot and advanced measurements

Ideal for rough unpolished diamonds or other samples without invading the microenvironment of the inclusion



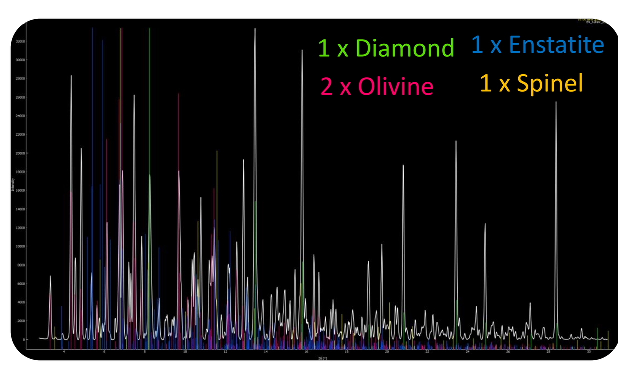
Large rotational collection
Minimum 70°, and even larger for low symmetry phases

Example 1 : A sublithospheric diamond contains several sub-surfaced inclusions. The user wants to characterize one of them before they decide if it is worth risking to expose it in the surface for further analysis.

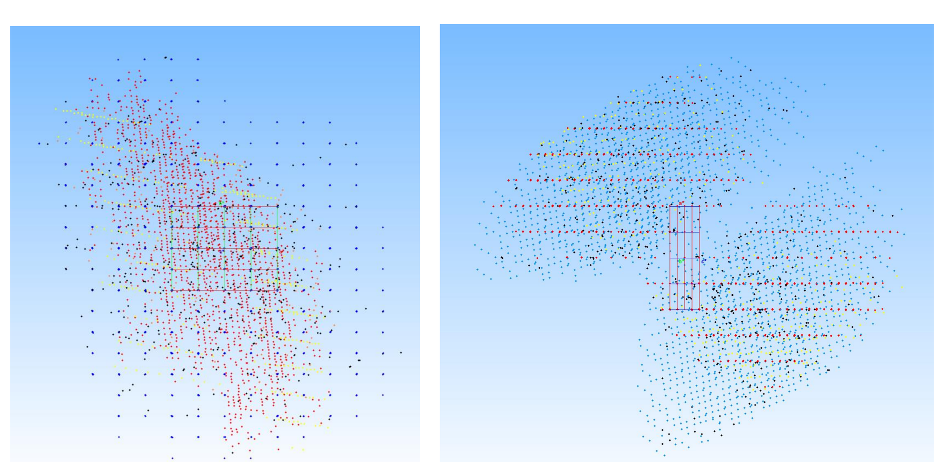


The inclusion of interest is clearly visible using X-ray imaging. The cross represents the X-ray beam position. We correct the XYZ position of the inclusion so that it remains under the X-ray during rotation.

The microstructure of the inclusion from the 3D reconstructed images.

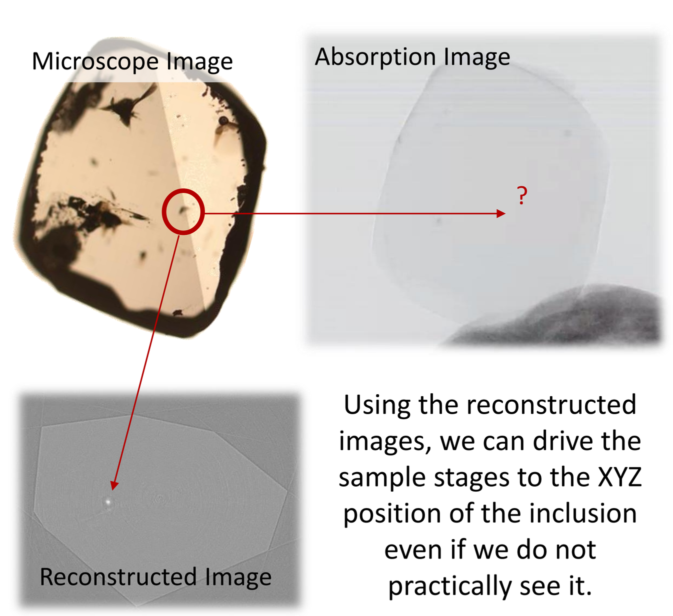


Conventional powder diffraction approach is not sufficient to deconvolute these complex XRD patterns.

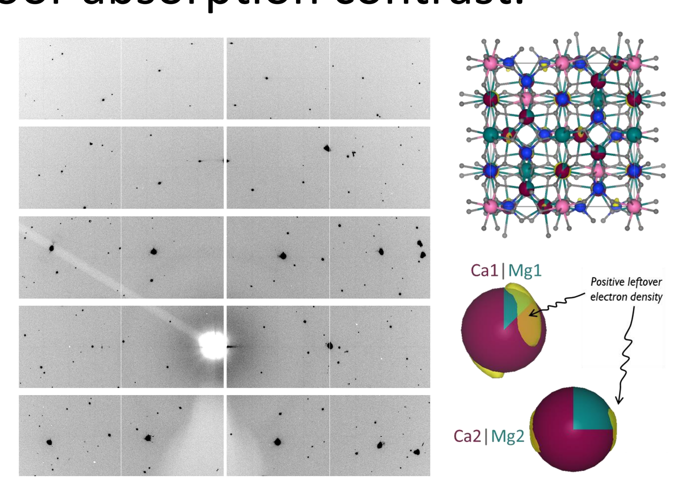


A single-crystal XRD approach on this multiphase/multigrain inclusion allows us to identify all the present phases and in the case of new mineral, solve its structure. Software like CrysAlis^{PRO} have excellent tools in untangling and reducing such datasets. Here we found reflections from 5 grains : diamond, enstatite, olivine and magnetite.

Example 2 : A user can see a subsurface inclusion under the microscope, but they can't see it using X-ray radiography, due to its low Z-elements content and poor absorption contrast.



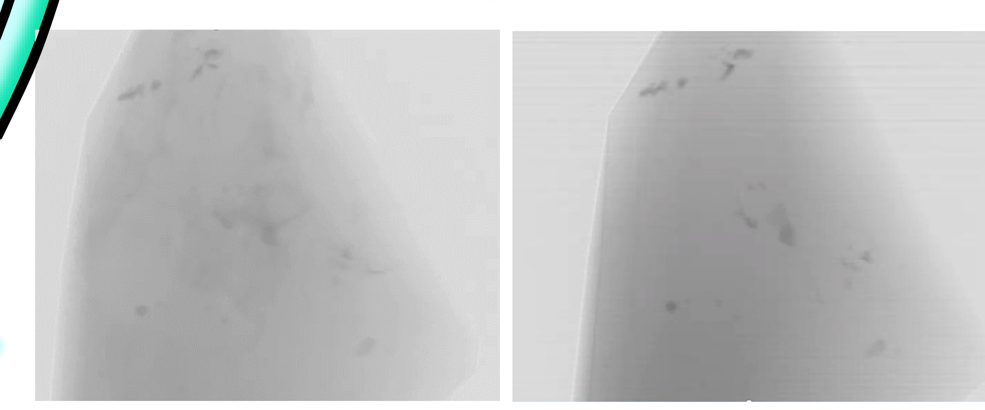
Using the reconstructed images, we can drive the sample stages to the XYZ position of the inclusion even if we do not practically see it.



SCXRD reveals that this is a majorite inclusion. SCXRD can aid with chemical characterization of few speculated elements (Ca, Mg), but leftover electron densities indicate that something is missing. The user must now decide to expose the inclusion and perform further analysis, such as EMPA.

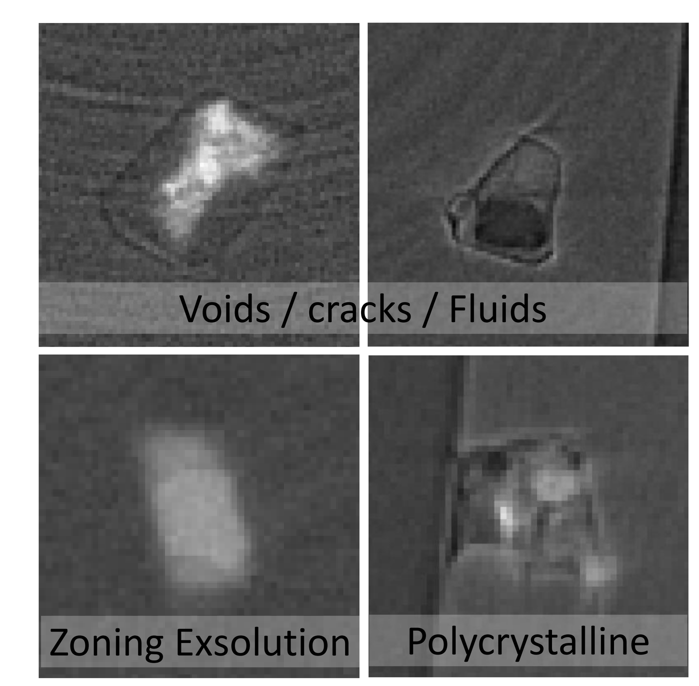
Monochromatic or pink beam for CMT?

Ask me for Videos!



Monochromatic Beam (37keV)	Pink Beam (30keV cutoff)
900 frames / 0.2° steps / 2 s exposure	1800 frames / 0.1° steps / 0.008 s exposure
Total Time: 31 min	**Total Time: < 1 min**

Other Features



3D reconstructions can help reveal sample features such as density contrast, cracks, zoning, fluid rims etc. Such macroscopic characteristics are important in describing the history of the inclusion.

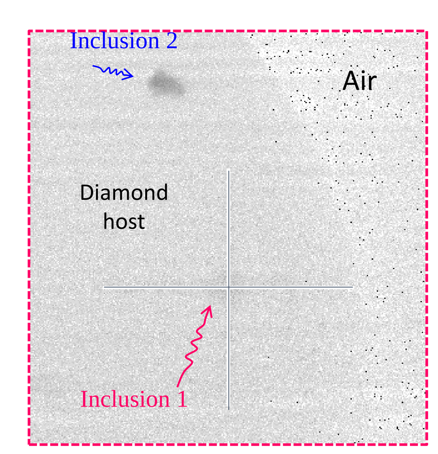
GeoSoilEnviroCARS is supported by the National Science Foundation – Earth Sciences via SEES: Synchrotron Earth and Environmental Science (EAR – 2223273). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

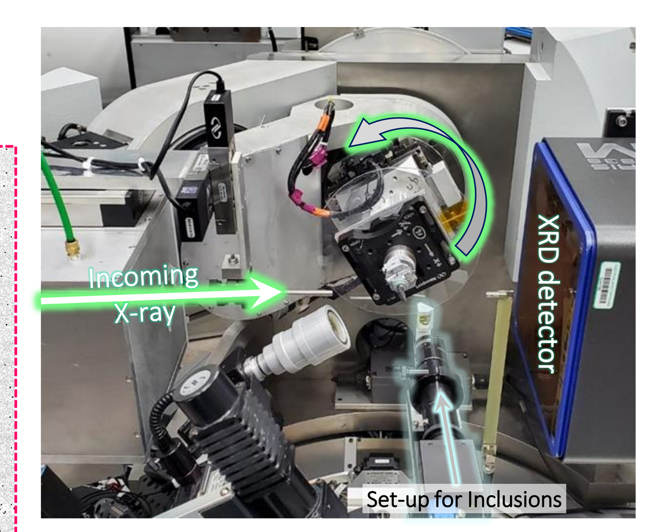
Contact: stellachariton@uchicago.du

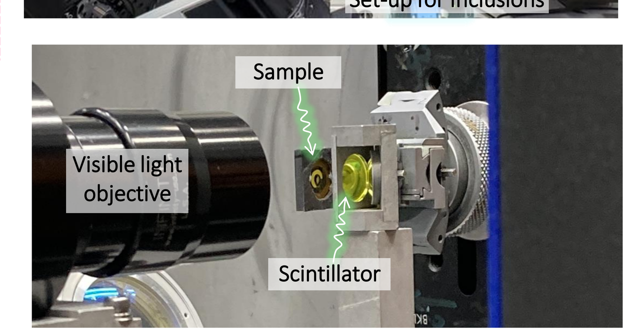
Other Techniques

The **13BM-C** beamline hosts a six-circle diffractometer and is ideal for SCXRD studies.

A portable camera system allows X-ray radiography experiments on diamond inclusions.







Although not of the same spatial resolution as CMT at 13BM-D, the user here can still locate and align on strongly or semi-absorbing inclusions. There is the extra benefit of multiple rotation axes which allows improved data completeness.