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Identification and structural characterization of mineralogical and cultural heritage related phases by synchrotron through-the-substrate microdiffraction technique

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Abstract

X-ray diffraction is a basic tool in the field of mineralogy, cultural heritage and material science that allows both the identification of crystalline phases and their structural determination. However, the characterization by X-ray diffraction is difficult when the phases of interest are not homogeneous, are small sized or are only present in very small regions of the sample. For this reason, a variant of the transmission microdiffraction technique called 'synchrotron through-the-substrate microdiffraction' (tts-μXRD) has been developed. This technique collect synchrotron diffraction data from a thin section of the sample mounted on a glass slide (Rius, 2011). The small beam diameter used in the experiment allows the acquisition of data from single phases (or from a reduced number of phases) directly on the thin section, thus preserving the textural information and avoiding the sample manipulation.

Keywords: Polished thin sections, Synchrotron tts-μXRD, X-ray data

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1. Introduction

Polished thin sections of rocks with the specimen fixed on a glass-substrate are commonly used in mineralogical, cultural heritage and material science studies. These sections are ideal for the microscope observation and for determining the optical properties. These studies are normally complemented with scanning electron microscope, electron microprobe or micro-Raman at a selected point of the polished thin sections. To complete the knowledge of a material, diffraction information of specific regions is often required. To this purpose, a new technique called through the substrate microdiffraction has been developed, which allows the direct measurement of polished thin sections in low volume phases of reduced areas. The small beam diameter (about 15μm) allows collecting data without the need of extracting the phases of interest from the thin section, thus preserving the textural context and avoiding possible sample deterioration during extraction of a fragment.

In tts-μXRD, the primary beam passes first through the glass substrate before reaching the thin section where the target material is embedded. This transmission geometry reduces the gauge volume variation during the diffraction experiment.

To study such systems synchrotron radiation is needed for its high penetration and associated Bragg angle compression and for the small spot size. Using a micro-visualization system, specific areas of interest from the sample can be selected and measured.

This technique it is easily applicable and ideal in the qualitative, textural and structural analysis of mineral associations.

2. Experimental setup

All the experiments were performed at the microdiffraction/high pressure station of the MSPD beamline (ALBA Synchrotron) (Fauth, 2013). This endstation is equipped with Kirkpatrick-Baezmirrors providing a monochromatic focused beam of 15 × 15 μm^2 (FWHM) size and a Rayonix SX165 CCD detector. The energy used in the experiments was 29.2 keV (λ = 0.4246 Å). The sample-detector distance (160–185 mm) and the beam centre positions were calibrated from LaB6 diffraction data measured at exactly the same conditions as the sample. The sample is placed in a xyz stage with a vertical tilt axis and it is visually mounted normal to the beam with the mineral in the thin-section always facing to the detector. The transparent glass-substrate allows selecting the measurement point directly with the coaxial microvisualization system (1).

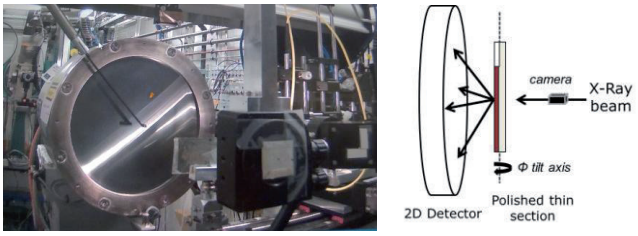

Fig. 1. Left: Experimental tts-μXRD setup at BL04 (ALBA synchrotron). Right: Schematic drawing

3. Applications

We show the validity of the technique using some representative examples in petrology and cultural heritage.

3.1 In-situ crystallographic study of the minerals associated to a blue pigment often used in mural painting

Aerinite is a blue pigment silicate associated with the alteration of tholeiitic diabases with an important cultural interest. In the study of the thin section containing aerinite a mineral with a different optical behaviour characterized by dark blue tonality was observed. The unknown mineral showed an abnormally high Si content compared to aerinite and it is emplaced forming a thin strip of about 100 μm embedded between the zeolites and aerinite (2). For this reason, it was decided to carry out the characterization using tts-μXRD in order to identify the mineral. The tts-μXRD measurements showed that it was in reality a mixture consisting of a monocrystalline phase with inclusions of aerinite fibres which were responsible for the blue colour. The 2D diffraction image (2) confirms the coexistence of the two crystalline phases and the unknown mineral was very well identified as Ca-K-rich chabasite.

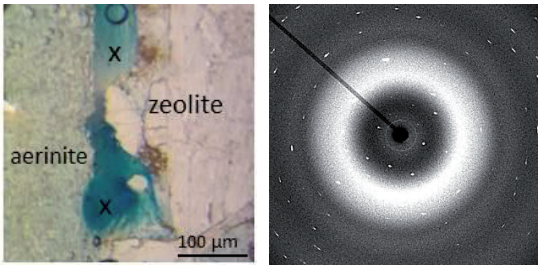

Fig. 2. Left: Photomicrograph of the polished thin section showing the mineral association formed by zeolite mixture of aerinite fibres and chabasite (X) and aerinite. Right: 2D image of the tts-μXRD pattern simultaneously showing the low angle Debye ring of aerinite and single spots of chabasite

3.2 Study of secondary phases present in archaeological ceramics

The second example is related to the study of the "golden slip" pottery type, at the site of Barikot (Swat Valley, north-western Pakistan) with the objective to understand the origin of the raw materials used. The slip is characterized by a thickness between 20 and 50 μm parallel to the ceramic body. The tts-μXRD technique was used to locally identify the minerals forming the golden slip and to do their mapping to observe the zonal distribution (300 μm x 1 mm) (3). The results of the local measurements showed an internal part of the ceramic body formed by quartz-rich paste and an external part of the golden slip characterized by oriented talc, enstatite and small amounts of forsterite. Using this new technique, information about distribution and texture of the minerals was obtained. Comparison of these results with those from conventional powder diffraction performed on mechanically separated slip parts, indicates that small amounts of secondary phases previously unnoticed, like forsterite, can now be observed (Maritan, 2018).

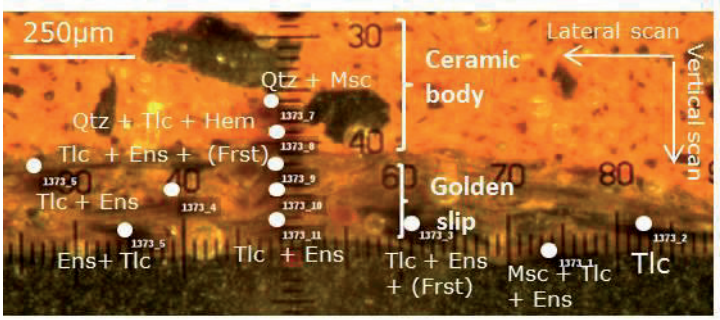

Fig. 3. Photo showing the mapping of the measurements (white circle) together with the corresponding identified phases (Tlc:Talc, Ens:Enstatite, Msc: Muscovite, Frst: Forsterite, Qtz: Quartz, Hem: Hematite)

3.3 Identification of small crystals formed in ceramic glazes

The crystalline precipitates formed in the decorations of glazes during their firing are responsible for the colour, shine, opacity among other visual characteristics of the decorations. The presence, distribution and growing habits of them give direct information about the materials and the production methods and can be used as a fingerprint of time, temperature, composition of the pigment and the glaze and the application methods. For this reason their identification is important. These micro-crystals are small-sized (about 10 µm) and very difficult to extract from the glass/glaze. This is why the tts-µXRD technique was applied.

In this example, a microcrystal had previously been identified by chemical techniques as a silicon oxide mineral, and the objective was to determine to which polymorph corresponded. This idiomorphic microcrystal (4) was measured at different points. Thanks to tts-µXRD technique it could be seen that the microcrystal was actually a mixture of quartz, cristobalite and trydimite phases (4).

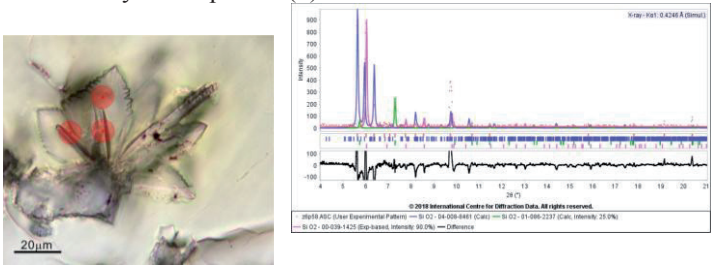

Fig. 4. Left: Selected microcrystal showing de local measurements. Right: Pattern diffraction of trydimite (blue), cristobalite (pink) and quartz (green)

4. Conclusions

The tts-µXRD technique provides data with enough quality to perform qualitative analysis of non homogeneous or/and small-sized areas as well as detailed refinements of crystalline phases only present as micro-volumes in the thin section. Moreover, it is easily

applicable and due to its non-destructive nature, it allows the same area to be studied later with other analytical techniques.

5. Acknowledgements

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