

3. METHODOLOGY

3.10.2.4. Variable amorphous content series

A constant matrix of calcite (C) and zincite (Z) was prepared. Five samples with increasing contents of amorphous ground glass (Gl) were then prepared. The elemental composition of the ground glass is given in García-Maté *et al.* (2014). The mixtures were labelled CZQ_*x*Gl, where *x* indicates 0, 2, 4, 8, 16 or 32 wt% Gl. The amorphous content was determined by adding ~20 wt% quartz (Q) as an internal standard.

3.10.3. Analytical techniques

All phases and mixtures were studied with Mo $K\alpha_1$ (transmission geometry) and Cu $K\alpha_1$ (reflection geometry) monochromatic radiation. Table 3.10.1 shows the X-ray linear absorption coefficients for all of the phases, as microabsorption is always a concern in ROPA. A microabsorption correction was not applied in this work, but readers must be aware that this effect, if relevant, is one of the greatest source of inaccuracy in ROPA (Madsen *et al.*, 2001; Scarlett *et al.*, 2002). All of the phases were also characterized by scanning electron microscopy (see Fig. 3.10.2).

3.10.3.1. Mo $K\alpha_1$ laboratory X-ray powder diffraction (LXRPD)

Mo $K\alpha_1$ powder patterns were collected in transmission geometry in constant irradiated volume mode, in order to avoid any correction of the measured intensities, on a D8 ADVANCE (Bruker AXS) diffractometer (188.5 mm radius) equipped with a Ge(111) primary monochromator, which gives monochromatic Mo radiation ($\lambda = 0.7093 \text{ \AA}$). The X-ray tube operated at 50 kV and 50 mA. The optics configuration was a fixed divergence slit (2°) and a fixed diffracted anti-scatter slit (9°). A LYNXEYE XE 500 μm energy-dispersive linear detector, optimized for high-energy radiation, was used with the maximum opening angle. Using these conditions, the samples were measured between 3 and $35^\circ 2\theta$ with a step size of 0.006° and with a total measurement time of 3 h 5 min. The flat samples were placed into cylindrical holders between two Kapton foils (Cuesta *et al.*, 2015) and rotated at a rate of 10 revolutions per minute during data collection. Moreover, the absorption factor of each sample was experimentally measured by comparing the direct beam with and without the sample (Cuesta *et al.*, 2015). The amount of sample loaded (which determines the height of the cylinder) in the holders was adjusted to obtain a total absorption (μt) of ~1, which corresponds to an absorption factor of ~2.7 or 63% of direct-beam attenuation. For the organic samples this criterion was not followed as it would lead to very thick specimens. In this case, the maximum holder thickness was used (1.7 mm).

3.10.3.2. Cu $K\alpha_1$ laboratory X-ray powder diffraction (LXRPD)

Cu $K\alpha_1$ powder patterns for exactly the same samples were recorded in reflection geometry ($\theta/2\theta$) on a X'Pert MPD PRO (PANalytical B.V.) diffractometer (240 mm radius) equipped with a Ge(111) primary monochromator, which gives monochromatic Cu radiation ($\lambda = 1.54059 \text{ \AA}$). The X-ray tube was operated at 45 kV and 40 mA. The optics configuration was a fixed divergence slit (0.5°), a fixed incident anti-scatter slit (1°), a fixed diffracted anti-scatter slit (0.5°) and an X'Celerator RTMS (real-time multiple strip) detector operating in scanning mode with the maximum active length. Using these conditions, the samples were measured between 6.5 and $81.5^\circ 2\theta$ with a step size of 0.0167° and a total measurement time of 2 h 36 min. The flat samples were prepared by rear charge of a flat sample holder in order to

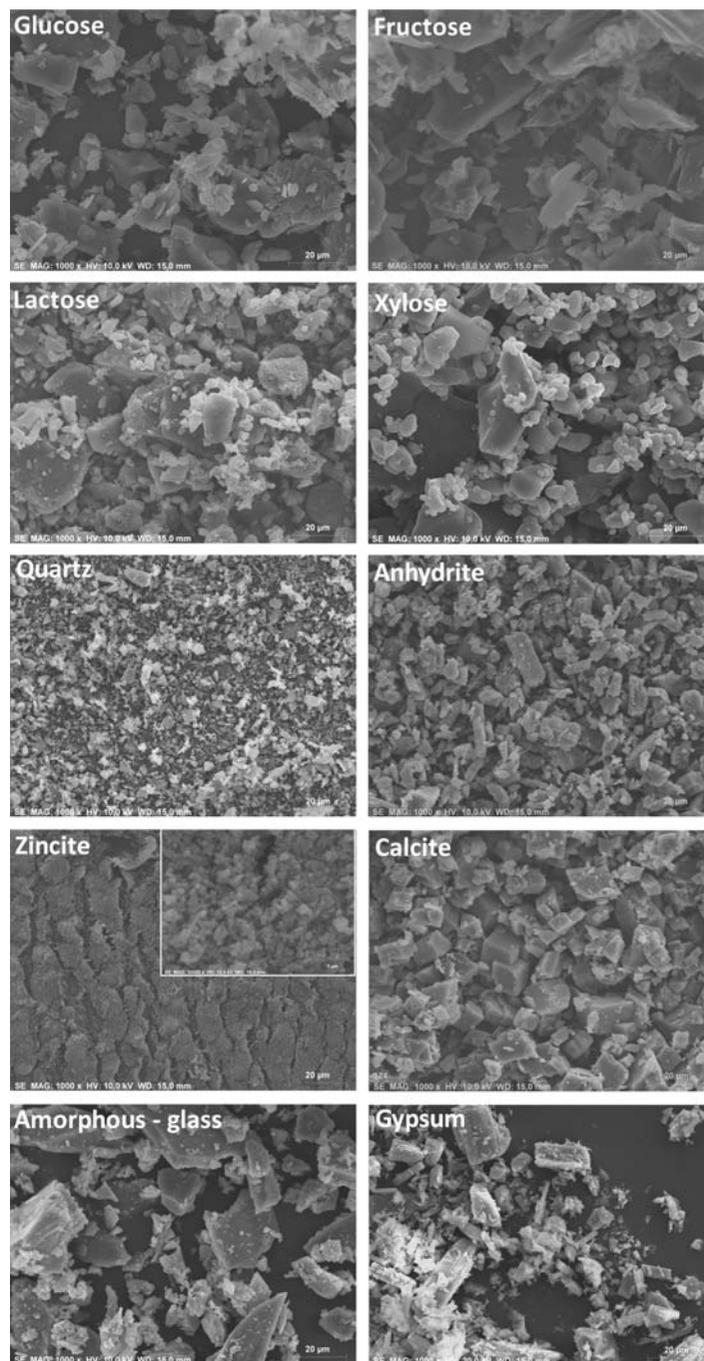


Figure 3.10.2

Scanning electron microscopy micrographs for the studied phases ($\times 1000$). The inset in the zincite micrograph shows the powder at higher magnification ($\times 20\,000$).

minimize preferred orientation and were rotated at a rate of 10 revolutions per minute.

The lowest analyte content samples, CGpQ_0.12A and GFL_0.12X, were measured three times using both radiations, Mo $K\alpha_1$ and Cu $K\alpha_1$, for a precision (reproducibility) assessment. Therefore, regrinding and reloading of the mixtures in the sample holder was carried out prior to every measurement.

3.10.3.3. Transmission synchrotron X-ray powder diffraction (SXRPD)

Powder patterns for the lowest analyte content samples, CGpQ_0.12A and GFL_0.12X, were also measured using synchrotron radiation. SXRPD data were collected in Debye–Scherrer (transmission) mode using the powder diffractometer at