

## 3. METHODOLOGY

**Table 3.10.2**Rietveld quantitative phase analyses for the crystalline inorganic mixtures measured with Cu  $K\alpha_1$  and Mo  $K\alpha_1$  radiations

Weighed amounts (wt%) are also shown for comparison. Absolute values of the Kullback–Liebler distance (AKLD) for each mixture and the KLD value for i-anhydrite are also included. Trm, transmission; rfl, reflection.

Phases	CGpQ_0.0A			CGpQ_0.25A			CGpQ_0.50A		
	wt%	Mo trm	Cu rfl	wt%	Mo trm	Cu rfl	wt%	Mo trm	Cu rfl
C	32.9	32.6 (1)	30.4 (2)	32.8	32.0 (1)	33.6 (1)	32.7	33.2 (1)	32.8 (1)
Gp	31.7	31.7 (1)	34.5 (1)	31.7	32.5 (1)	31.6 (1)	31.6	30.1 (1)	30.7 (1)
Q	34.2	34.6 (1)	33.7 (1)	34.1	33.9 (1)	33.0 (1)	34.0	34.6 (1)	34.2 (1)
s-A	0.8	0.66 (3)	0.76 (5)	0.8	0.77 (4)	0.78 (5)	0.8	0.97 (3)	1.15 (5)
SrSO <sub>4</sub>	0.4	0.44 (4)	0.70 (6)	0.4	0.44 (4)	0.67 (5)	0.4	0.39 (4)	0.56 (5)
i-A	—	—	—	0.28	0.42 (3)	0.42 (4)	0.52	0.71 (3)	0.71 (4)
AKLD sum		0.0089	0.0605		0.0198	0.0235		0.0295	0.0180
(i-A) KLD					−0.001	−0.001		−0.002	−0.002

Phases	CGpQ_1.0A			CGpQ_2.0A			CGpQ_4.0A		
	wt%	Mo trm	Cu rfl	wt%	Mo trm	Cu rfl	wt%	Mo trm	Cu rfl
C	32.5	32.8 (1)	32.6 (2)	32.2	31.3 (1)	31.4 (1)	31.6	31.2 (1)	31.8 (1)
Gp	31.5	30.4 (1)	30.7 (1)	31.1	32.1 (1)	32.3 (1)	30.5	30.7 (1)	30.5 (1)
Q	33.8	34.1 (1)	33.8 (1)	33.5	33.5 (1)	32.6 (1)	32.8	32.8 (1)	32.0 (1)
s-A	0.8	1.03 (4)	1.11 (5)	0.7	0.54 (3)	0.58 (5)	0.7	0.67 (3)	0.77 (4)
SrSO <sub>4</sub>	0.4	0.43 (4)	0.68 (5)	0.4	0.48 (4)	0.68 (6)	0.4	0.45 (4)	0.63 (5)
i-A	1.02	1.23 (3)	1.17 (5)	2.02	2.05 (4)	2.38 (9)	4.02	4.30 (8)	4.33 (9)
AKLD sum		0.0214	0.0152		0.0218	0.0358		0.0095	0.0156
(i-A) KLD		−0.002	−0.001		0.000	−0.003		−0.004	−0.003

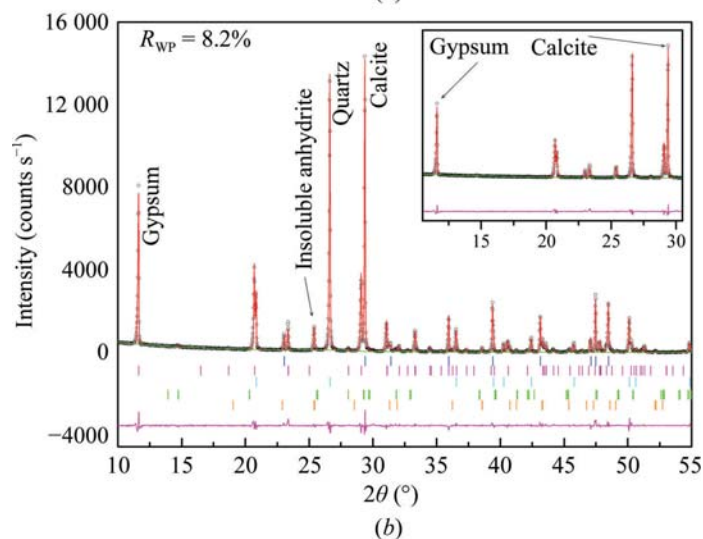
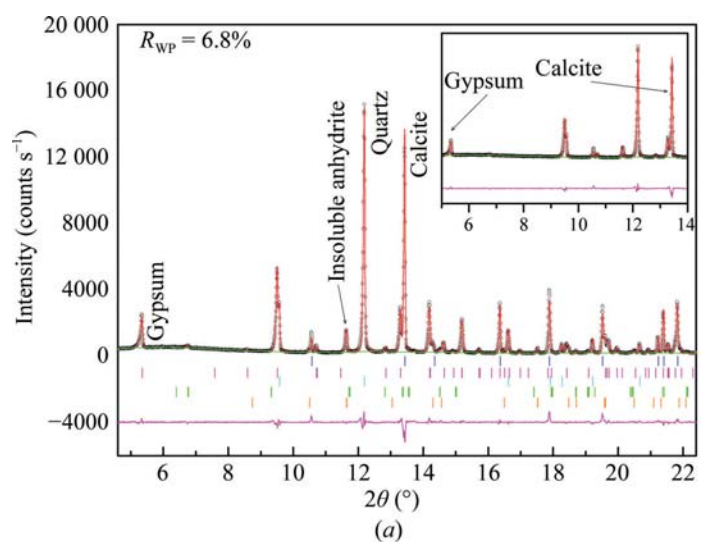
**Figure 3.10.6**Selected range of the Rietveld plots for CGpQ\_4.0A: (a) Mo  $K\alpha_1$  and (b) Cu  $K\alpha_1$  patterns. The inset highlights the effect of preferred orientation for gypsum and calcite.

Fig. 3.10.5 shows Mo  $K\alpha_1$  and Cu  $K\alpha_1$  raw patterns of the organic mixtures with increasing amounts of xylose. The strongest powder-diffraction peak for xylose in the GFL\_0.12X patterns (with both Mo and Cu radiations) was not observed. The corresponding peak was observed in the GFL\_0.25X patterns. Therefore, the LoD can be established as close to 0.25 wt%. The analysis results for xylose in GFL\_0.25X were reported in León-Reina *et al.* (2016). These values showed that the results from Mo  $K\alpha_1$  powder diffraction were slightly more accurate.

The LoQ for xylose was also studied. Once again, three Mo  $K\alpha_1$  and Cu  $K\alpha_1$  patterns were collected for GFL\_0.12X. The average value for the analysis of the three Mo patterns was 0.18 (8) wt%. Similarly, the average result for the analyses of three Cu patterns was 0.34 (6) wt%. Full RQPA results are reported in the supporting information of León-Reina *et al.* (2016). The LoQ for xylose in this mixture for the two radiations can be established as close to 0.12 wt%. Indeed, if one applies an ‘acceptable reliability’ criterion, the LoQ would be much higher at above 1 wt%. The output of this study was that Cu  $K\alpha_1$  radiation yielded a slightly less accurate result than that obtained from the Mo  $K\alpha_1$  data.

GFL\_0.12X was also studied by SXRPD in a rotating glass capillary in transmission mode. Fig. 3.10.5(c) shows SXRPD patterns for GFL\_0.12X collected at three different positions of the same capillary. The powder patterns showed quite different peak ratios. It is important to bear in mind that filling a glass capillary with organic compounds is sometimes not easy due to electrostatic charge effects. For this reason, the phase ratio within the part of capillary bathed by the X-rays might not be the same as that of the sample under study. The behaviour observed in Fig. 3.10.5(c) could be explained by inhomogeneous capillary filling. Hence, in this case, the RQPA results are unreliable. Even in ‘well behaved’ samples, inhomogeneous filling of small capillaries could result in problems. Readers should be aware of this, and the authors strongly recommend that at least three patterns should be collected along the capillary and superimposed. If there is inhomogeneous filling the patterns will differ, and extreme care