Electronic Supplementary Material (ESI) for Dalton Transactions

In-situ EDXRD Study of the Chemistry of Aging of Co-precipitated Mixed Cu,Zn Hydroxycarbonates – Consequences for the Preparation of Cu/ZnO Catalysts

Supporting Information

*Stefan Zander, Beatrix Seidlhofer, Malte Behrens**

**behrens@fhi-berlin.mpg.de*

Table S1: Aging parameters and internal sample numbers. The sample ID 0 refers to the unaged precursor.

ID	pH	T [K]	A^+ in A_2CO_3	FHI sample number[a]
0	-	-	-	7005
1	5	333	Na^+	7037
2	6	333	Na^+	7057
3	6.5	333	Na^+	7064
4	7	333	Na^+	7045
5	7.5	333	Na^+	7036
6	8	333	Na^+	7038
7	7	323	Na^+	7044
8	7	343	Na^+	7043
9	7	333	K^+	7063
10	7	343	K^+	7058

[a] To facilitate sample identification and communication, please refer to these labels upon correspondence.

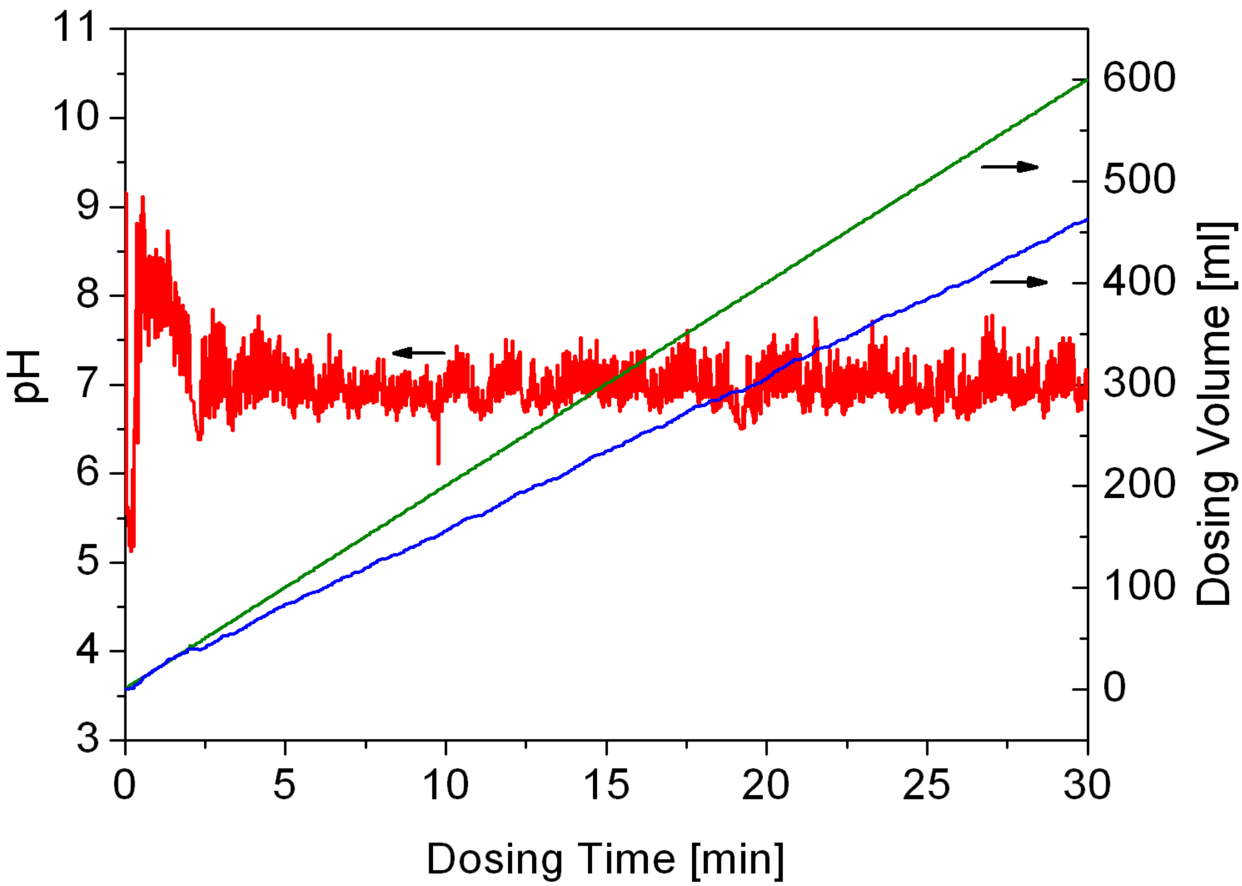

Figure S1: Evolution of pH (red curve) with added Cu,Zn solution (green curve) and Na_2CO_3 solution (blue curve) during co-precipitation of the Cu,Zn (70:30) precursor in the continuous process. The slurry was continuously fed into a spray-dryer.

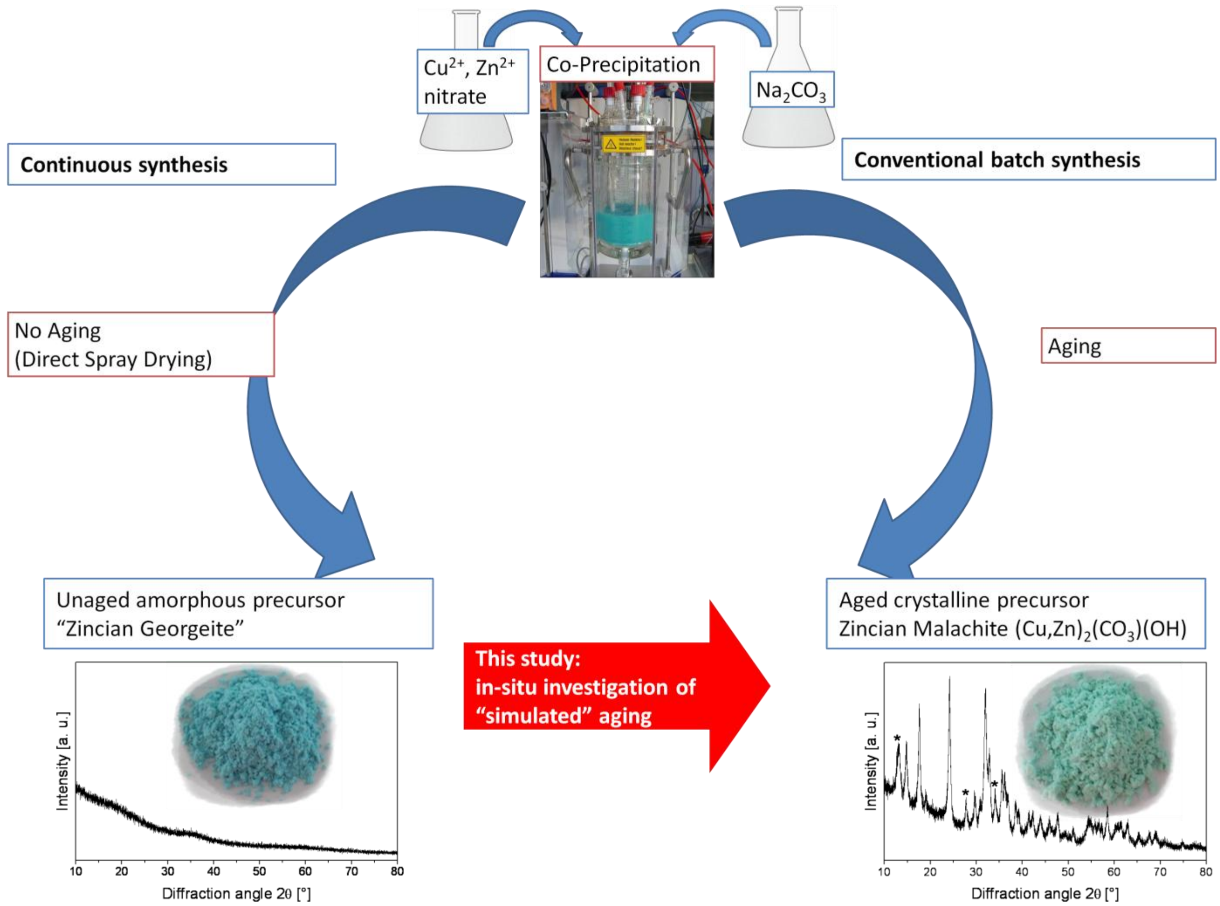

Figure S2: Schematic representation for the T- and pH-controlled precursor preparation from aqueous solutions using an automated laboratory-reactor. The co-precipitation and aging stages (right hand side) were decoupled by continuously removing the "unaged" precursor (left hand side) and subsequent aging studies at varying conditions with the same starting material (red arrow). The marked reflections in the lower right hand corner XRD pattern refer to the aurichalcite by-phase, $(Cu,Zn)_5(CO_3)_2(OH)_6$. All other reflection are due to zincian malachite $(Cu,Zn)_2(OH)_2CO_3$. The batch-aged precursor yields a Cu/ZnO catalyst with an approximate activity of 0.7 $kg_{MeOH}\ h^{-1}\ g_{cat}^{-1}$.

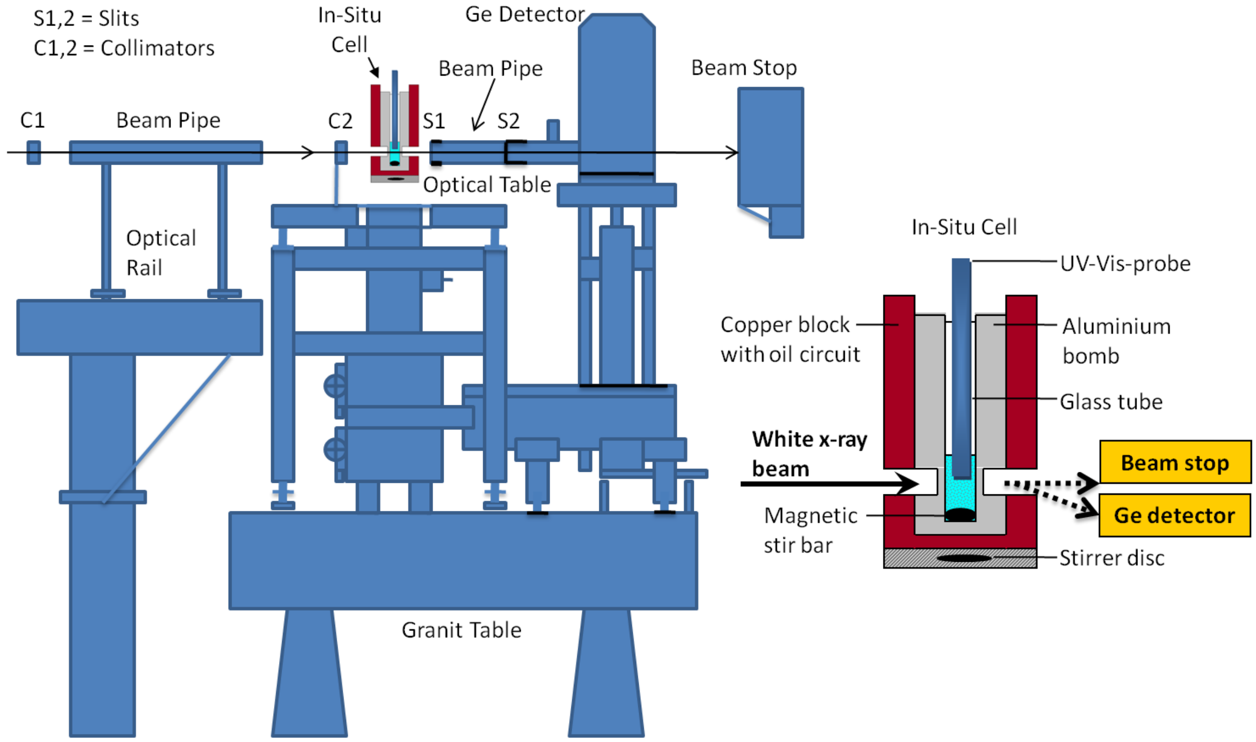

Figure S3: Detailed experimental setup of *in-situ* EDXRD reaction cell at the F3 beamline at HASYLAB, Hamburg, Germany.

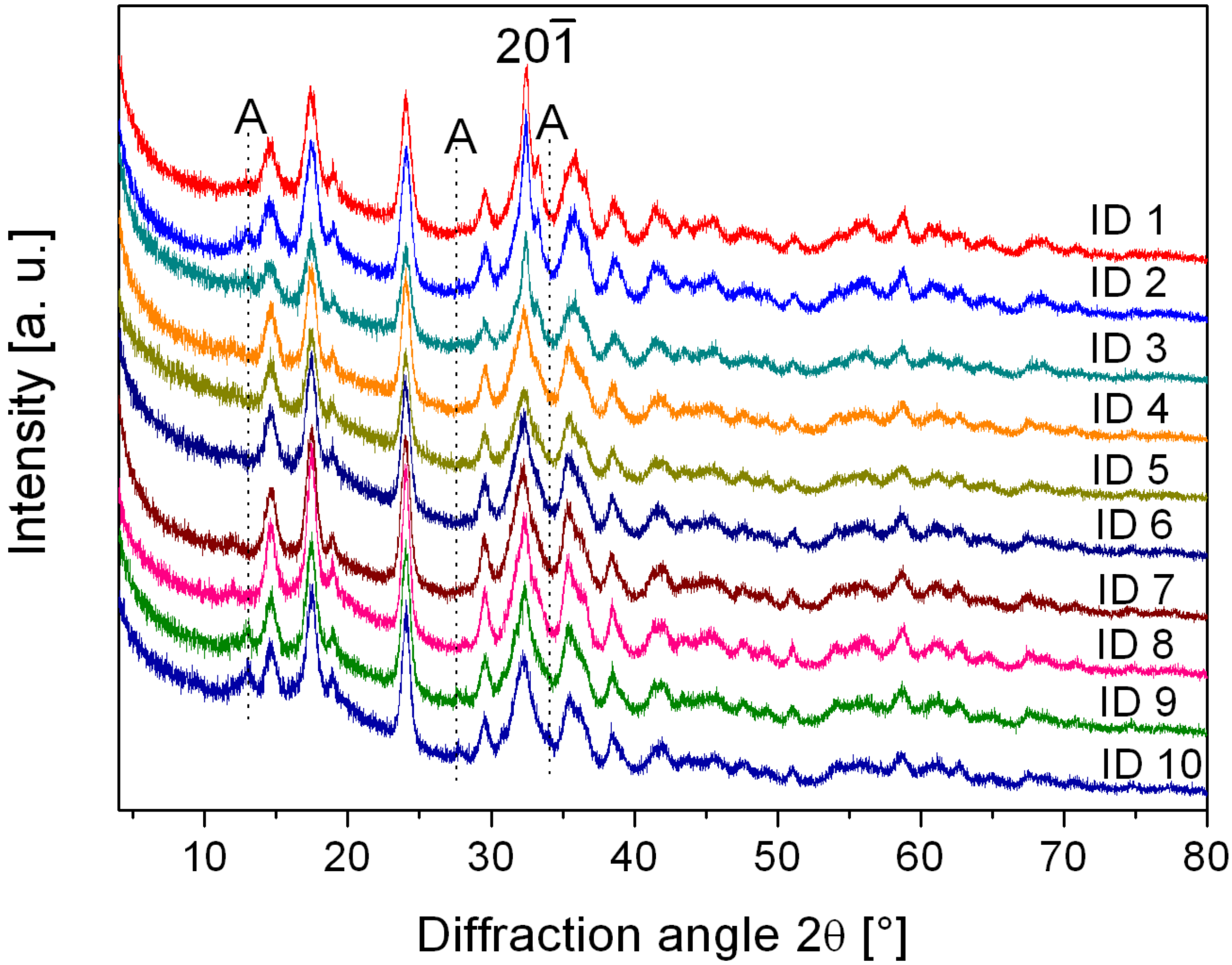

Figure S4: *Ex-situ* XRD patterns of all recovered sample (for labeling see Tab. 1). The $20\bar{1}$ reflection of malachite and the characteristic peaks of aurichalcite are marked. The labeling refers to the entry number of Table 1 in the main article.

Table S2: SEM-EDX results of unaged precursor (ID 0) and aged precursors (ID 1, 6).

	ID 0 (unaged)		**ID 1 (aged pH 5.0)**		**ID 6 (aged pH 8.0)**	
	Cu [mol-%]	Zn [mol-%]	Cu [mol-%]	Zn [mol-%]	Cu [mol-%]	Zn [mol-%]
Area 1	70.95	29.05	70.84	29.16	70.71	29.29
Area 2	70.23	29.77	70.11	29.89	69.71	30.29
Area 3	71.12	28.88	70.45	29.55	70.7	29.3
Area 4	71.15	28.85	70.91	29.09	70.59	29.41
Area 5	70.79	29.21	71.24	28.76	69.1	30.9
Average ± STD	**70.8 ± 0.4**	**29.2 ± 0.4**	**70.7 ± 0.4**	**29.3 ± 0.4**	**70.2 ± 0.7**	**29.8 ± 0.7**

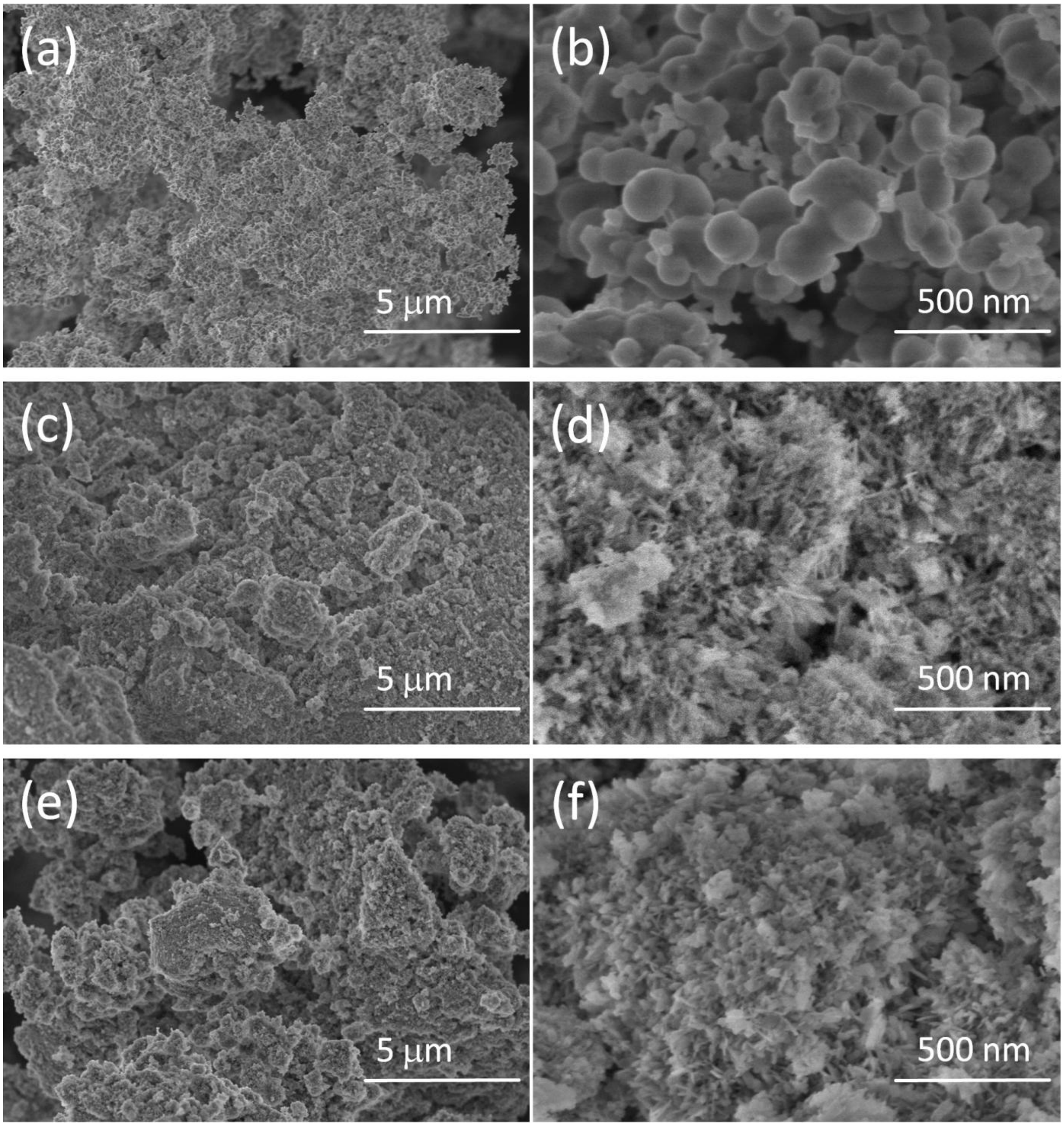

Figure S5: SEM images of unaged precursor, ID 0 (a,b) and aged precursors, ID 1 (c,d) and ID 6 (e,f).

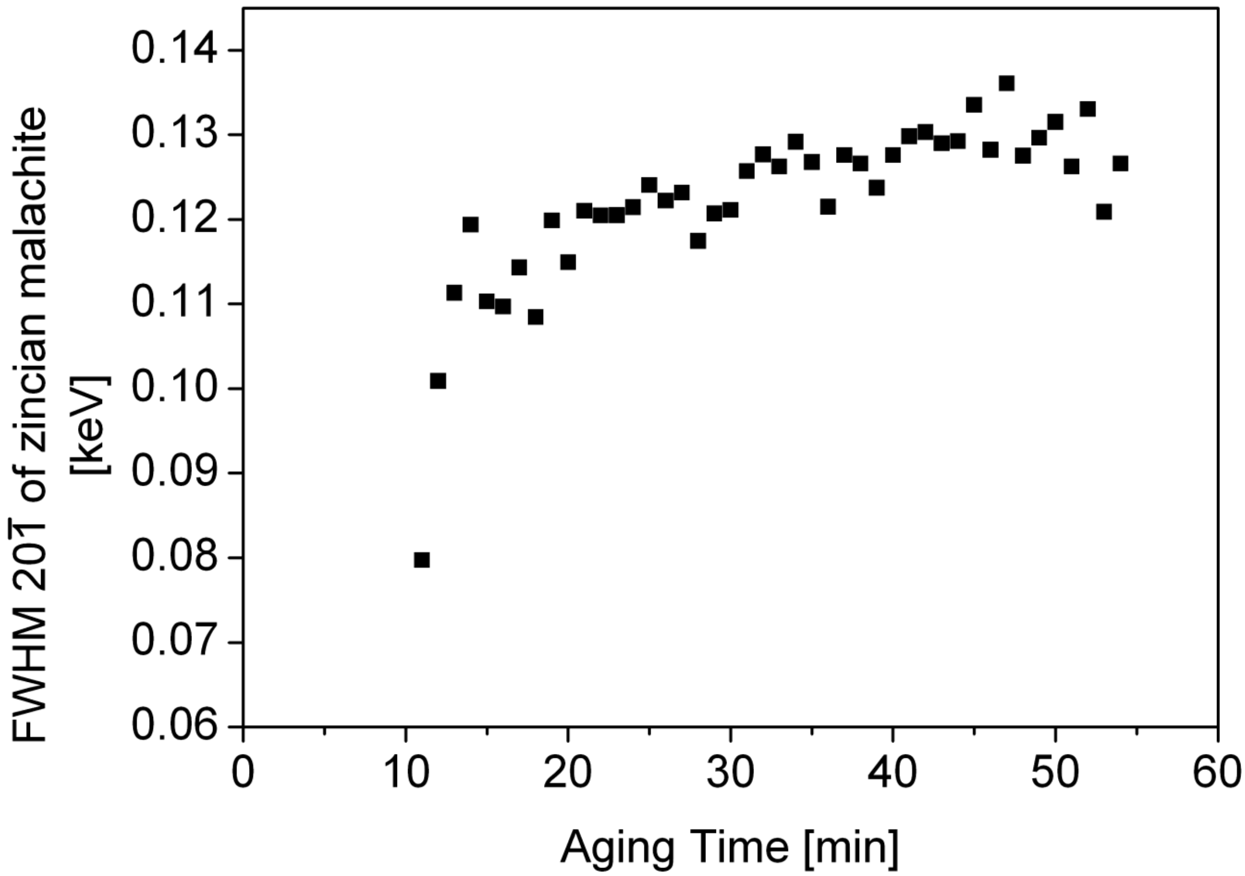

Figure S6: Evolution of the FWHM of the 20$\bar{1}$ peak of zincian malachite from the EDXRD spectra during simulated aging at pH 7, 323 K (ID 7). In all aging experiment where reflections of the sodium zinc intermediate were detected, the FWHM of the 20$\bar{1}$ peak of zincian malachite did not decrease during disappearance of the sodium zinc carbonate phase. Thus, the shift of the 20$\bar{1}$ peak seems not to be an effect of overlapping peaks from both phases but rather of Zn incorporation into the zincian malachite phase.

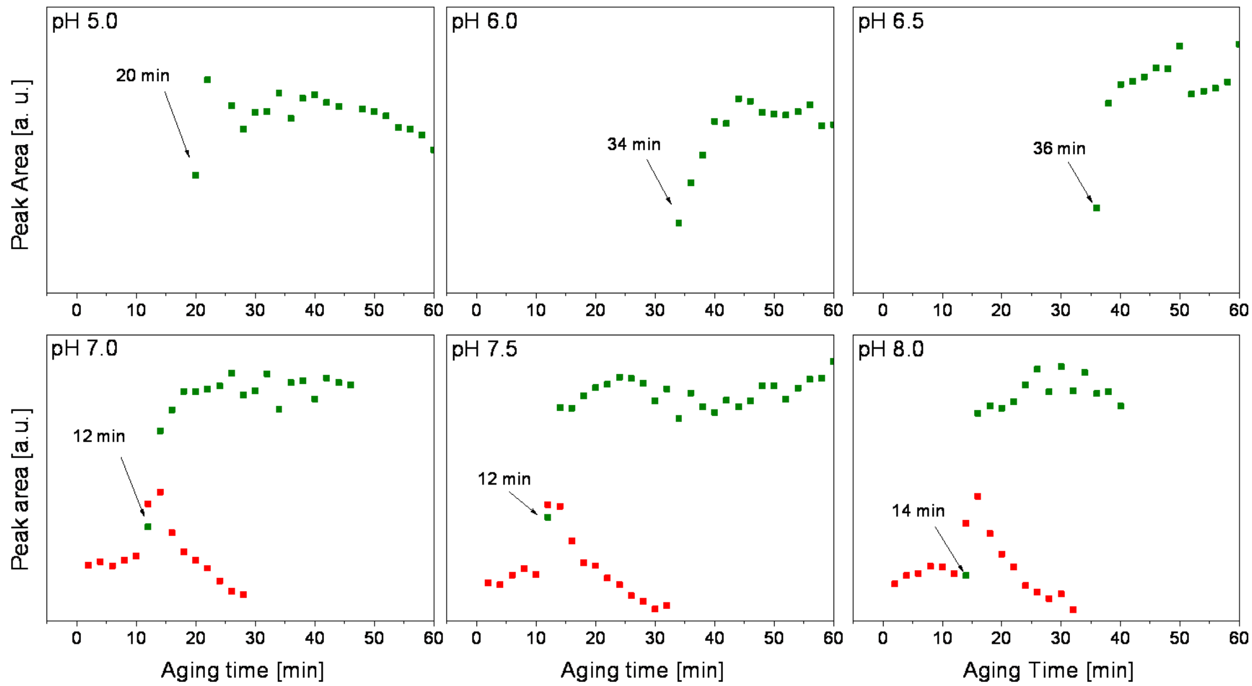

Figure S7: Integral intensity of selected EDXRD peaks of detected phases vs. aging time in Na_2CO_3 at T = 333 K at different pH-values. Zincian malachite $(Cu,Zn)_2(OH)_2(CO_3)$ is represented by the $20\bar{1}$ peak (green), sodium zinc carbonate $Na_2Zn_3(CO_3)_4\cdot 3H_2O$ is represented by the 222 peak (red).