Supplementary Information

Reversible sorption of carbon dioxide in Ca-Mg-Fe systems for thermochemical energy storage applications

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Table S1. Description of the natural ankerite samples.

Sample ID	Geographic origin	Mineral description
Ankerite-1	Tansifite Caïdat, Agdz Cercle, Zagora Province, Drâa-Tafilalet Region, Morocco	Devilline and selenite on ankerite
Ankerite-2	Binn Valley, Valais, Switzerland (Turb Alp)	Goethite pseudo after ankerite
Ankerite-3	Spain	Ankerite

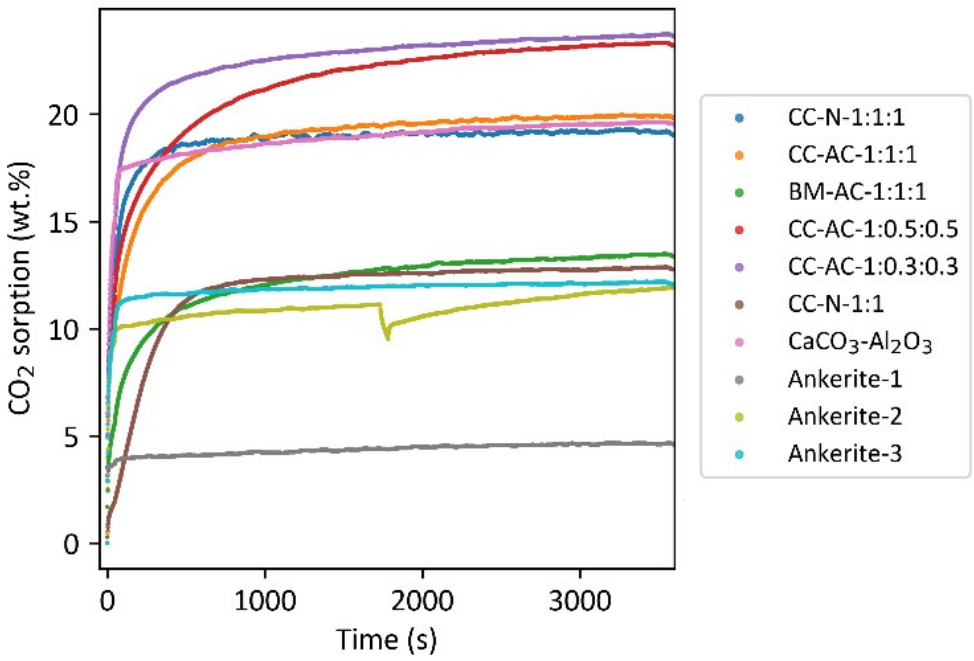

Figure S1. Evolution of the CO_2 wt.% absorption over time during the first cycle.

Table S2. Quantitative analysis of the sample composition of $CaCO_3$-Al_2O_3 (20 wt.%) before and after 100 cycles at 750 °C (1 h vacuum desorption / 1 h absorption at 5 bar CO_2).

Composition (%)	**$CaCO_3$**	**Al_2O_3**	**Hydrated Al_2O_3**	**$CaMg(CO_3)_2$**	**CaO**	**$Ca_5Al_6O_{14}$**	**$Ca_9Al_6O_{18}$**	**$CaAl_{12}O_{19}$**
Initial	79.4(4)	16.0(4)	0.2(7)	4.5(2)	-	-	-	-
After 100 cycles at 750 °C	50.1(1)	18.8(4)	-	-	15.0(3)	4.6(7)	10.3(2)	1.2(3)

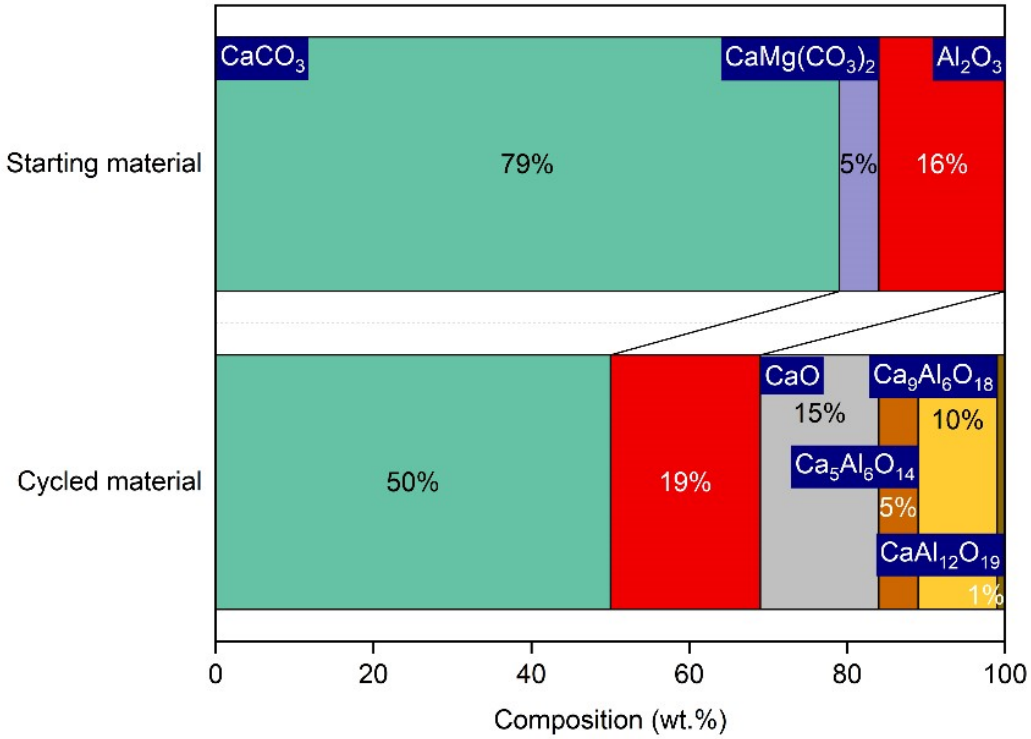

Figure S2. Composition of the $CaCO_3$-Al_2O_3 (20 wt.%) before and after 100 cycles at 750 °C with 1 h vacuum desorption and 1 h absorption at 5 bar CO_2. The samples are in the carbonated state and the XRD patterns are presented in Figure S3 and Figure S4.

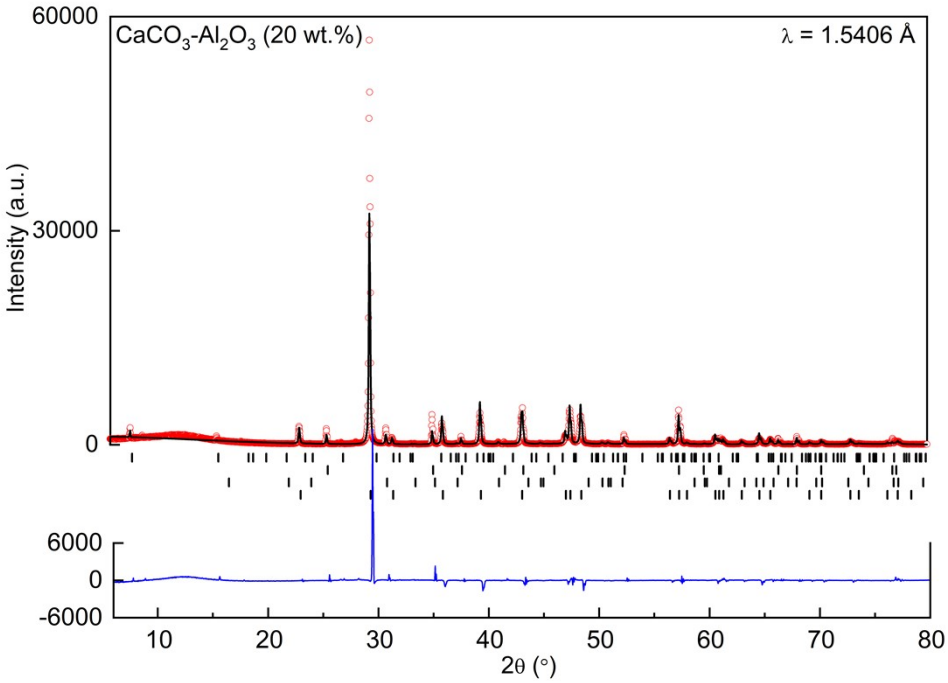

Figure S3. XRD pattern and fitting curve of the Rietveld refinement of $CaCO_3$-Al_2O_3 (20 wt.%). Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, Dolomite, Al_2O_3 and hydrated Al_2O_3, bottom to top, respectively.

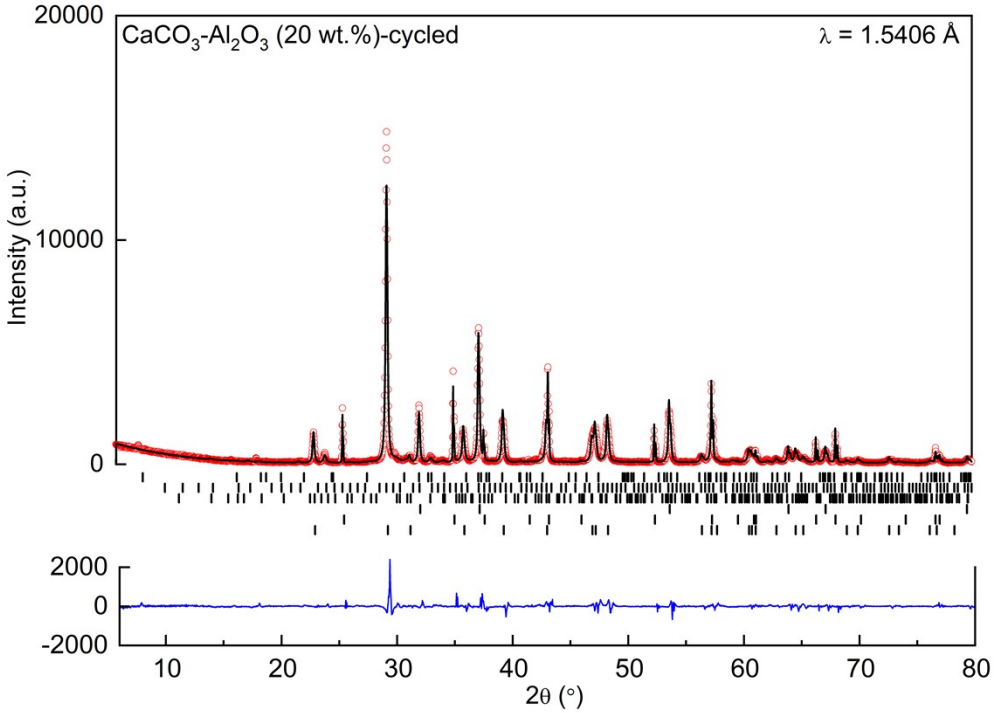

Figure S4. XRD pattern and fitting curve of the Rietveld refinement of cycled $CaCO_3$-Al_2O_3 (20 wt.%). Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, Al_2O_3, CaO, $Ca_5Al_6O_{14}$, $Ca_9Al_6O_{18}$ and $CaAl_{12}O_{19}$, bottom to top, respectively.

Table S3. Quantitative analysis of the sample composition of the natural ankerite samples.

Composition (%)	**$Ca(Mg,Fe)(CO_3)_2$**	**$CaSO_4$**	**$CaCO_3$**	**SiO_2**	**FeO(OH)**
Ankerite-1	85.8(2)	14.2(2)	-	-	-
Ankerite-2	-	-	55.6(1)	-	44.4(1)
Ankerite-3	67.0(2)	-	-	33.0(2)	-

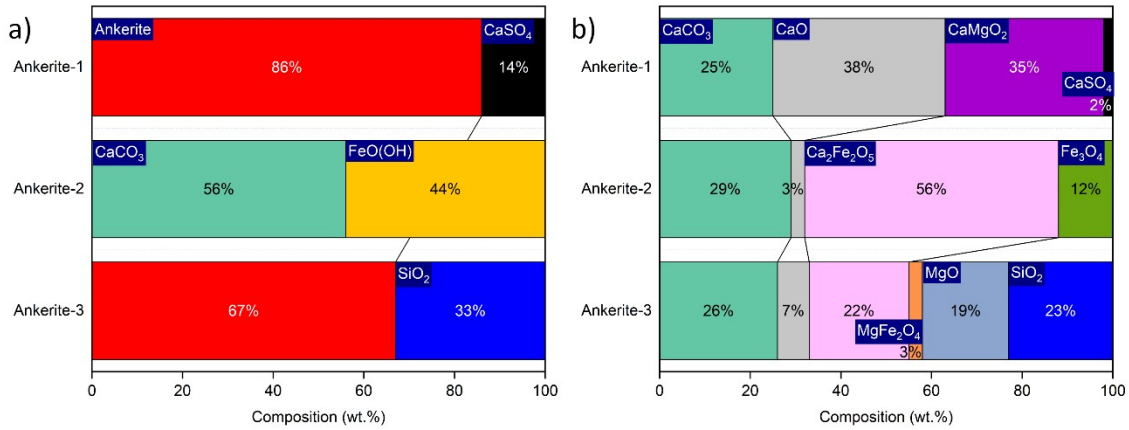

Figure S5. Quantitative composition determined by Rietveld refinement of: (a) the natural Ankerite samples and (b) after 100 cycles at 750 °C with 1 hour vacuum desorption and 1 hour absorption at 5 bar CO_2. All samples are in the carbonated state and the SR-XRD patterns are presented in Figure S6 to Figure S11.

Table S4. Quantitative analysis of the sample composition of the natural ankerite samples after 100 cycles at 750 °C (1 h vacuum desorption / 1 h absorption at 5 bar CO_2).

Composition (%)	$CaCO_3$	CaO	CaMgO	$CaSO_4$	$Ca_2Fe_2O_5$	Fe_3O_4	MgO	$MgFe_2O_4$	SiO_2
Ankerite-1	25.2(1)	38.0(1)	34.6(1)	2.2(1)	-	-	-	-	-
Ankerite-2	28.5(1)	3.2(5)	-	-	56.1(1)	12.3(8)	-	-	-
Ankerite-3	25.7(9)	7.0(4)	-	-	-	-	19.2(9)	3.4(4)	23.5(8)

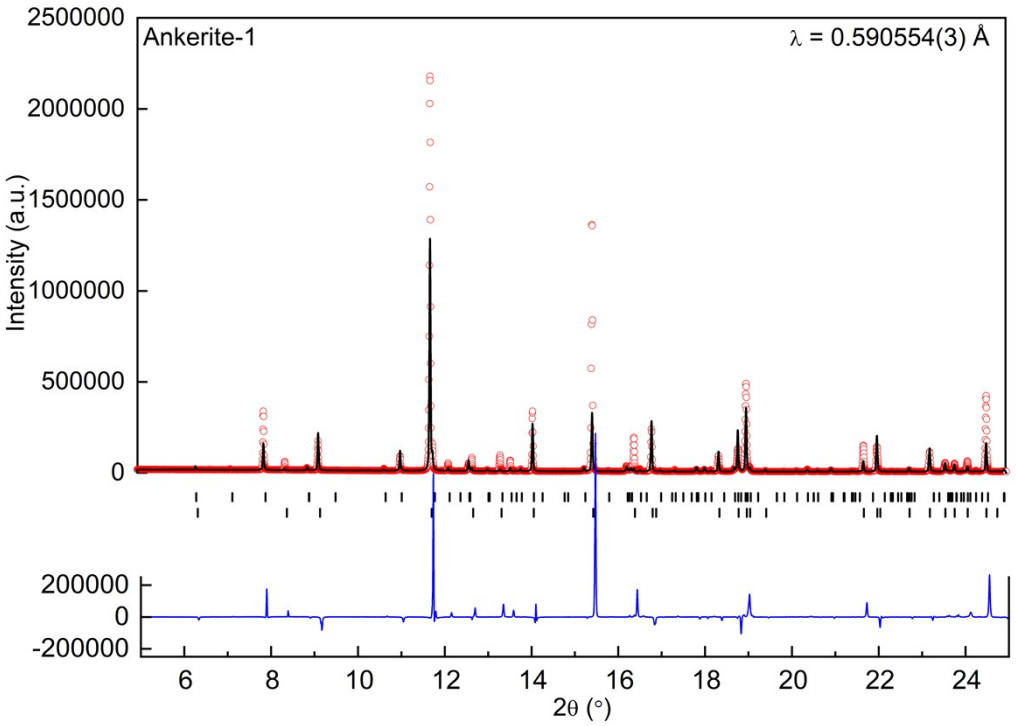

Figure S6. XRD pattern and fitting curve of the Rietveld refinement of natural Ankerite-1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: Ankerite and Gypsum, bottom to top, respectively.

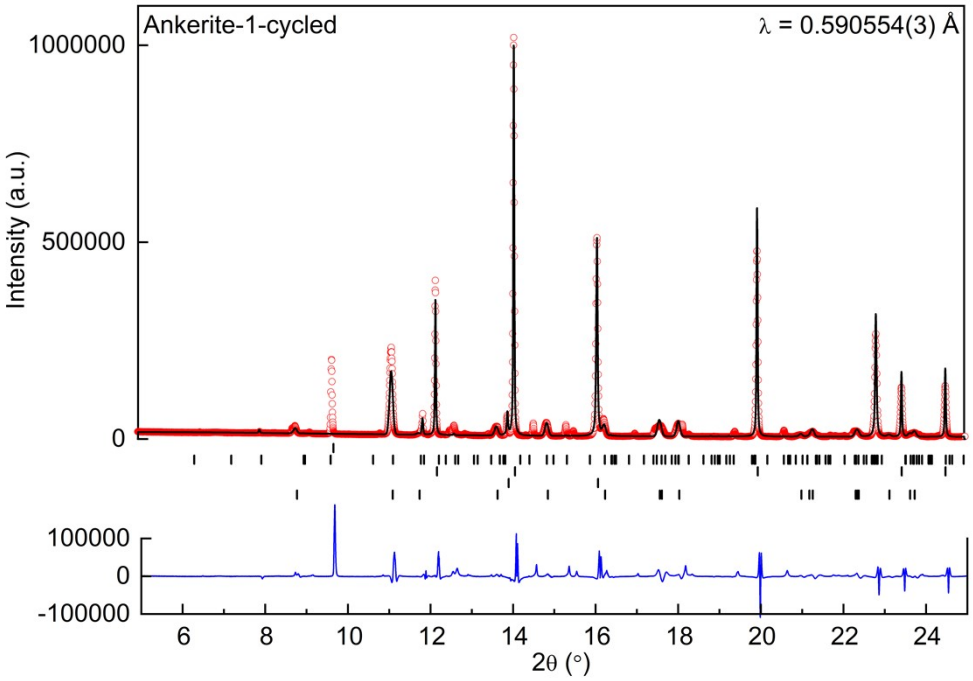

Figure S7. XRD pattern and fitting curve of the Rietveld refinement of cycled Ankerite-1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, CaMgO, CaO, Gypsum and an unknown peak, bottom to top, respectively.

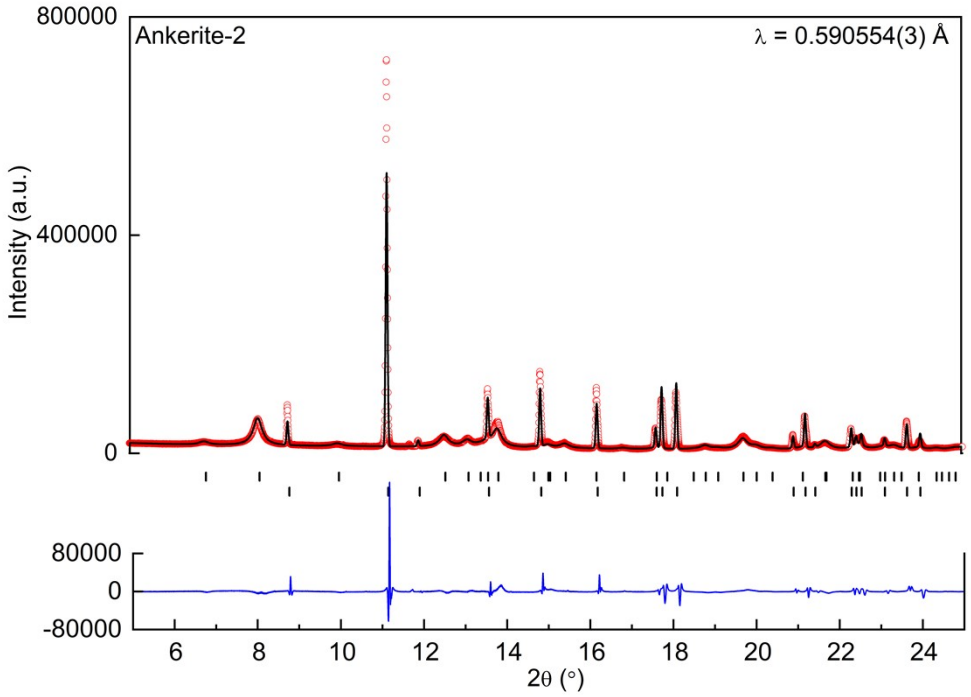

Figure S8. XRD pattern and fitting curve of the Rietveld refinement of natural Ankerite-2. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$ and FeO(OH), bottom to top, respectively.

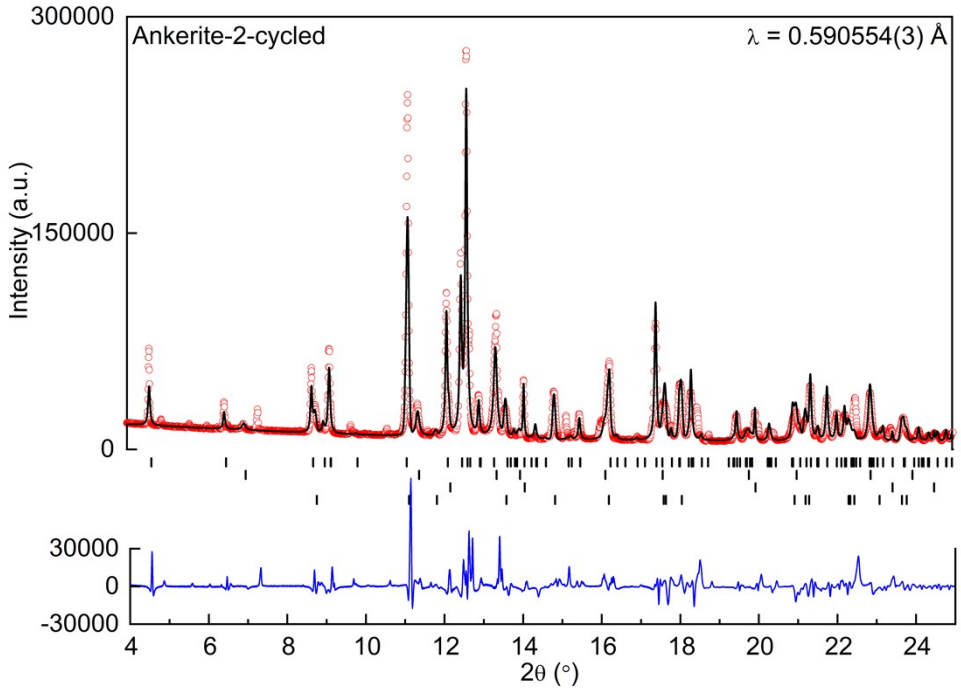

Figure S9. XRD pattern and fitting curve of the Rietveld refinement of cycled Ankerite-2. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, CaO, Fe_3O_4 and $Ca_2Fe_2O_5$ bottom to top, respectively.

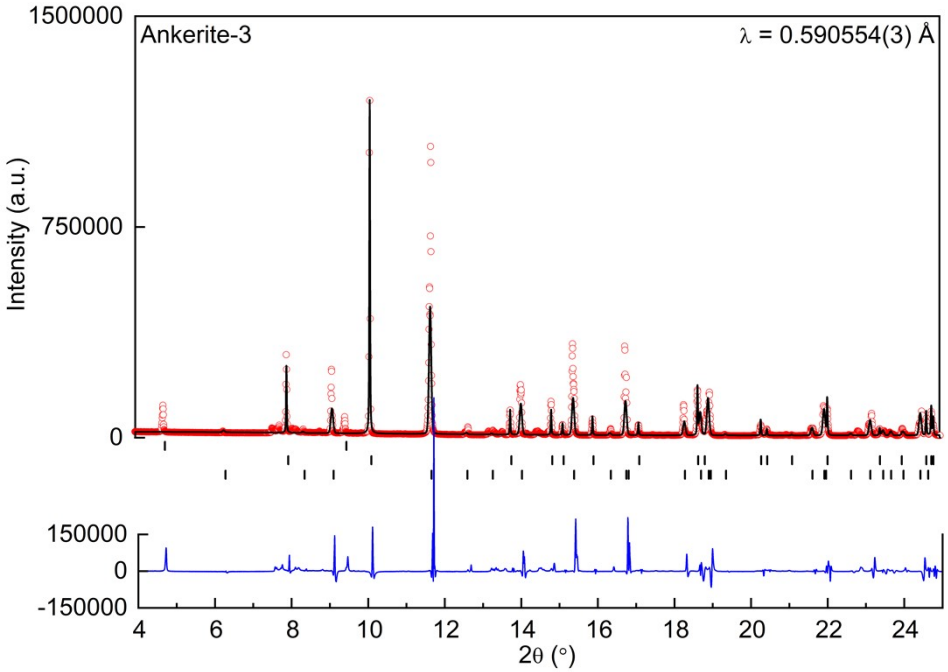

Figure S10. XRD pattern and fitting curve of the Rietveld refinement of natural Ankerite-3. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: Ankerite, Quartz, and an unknown phase bottom to top, respectively.

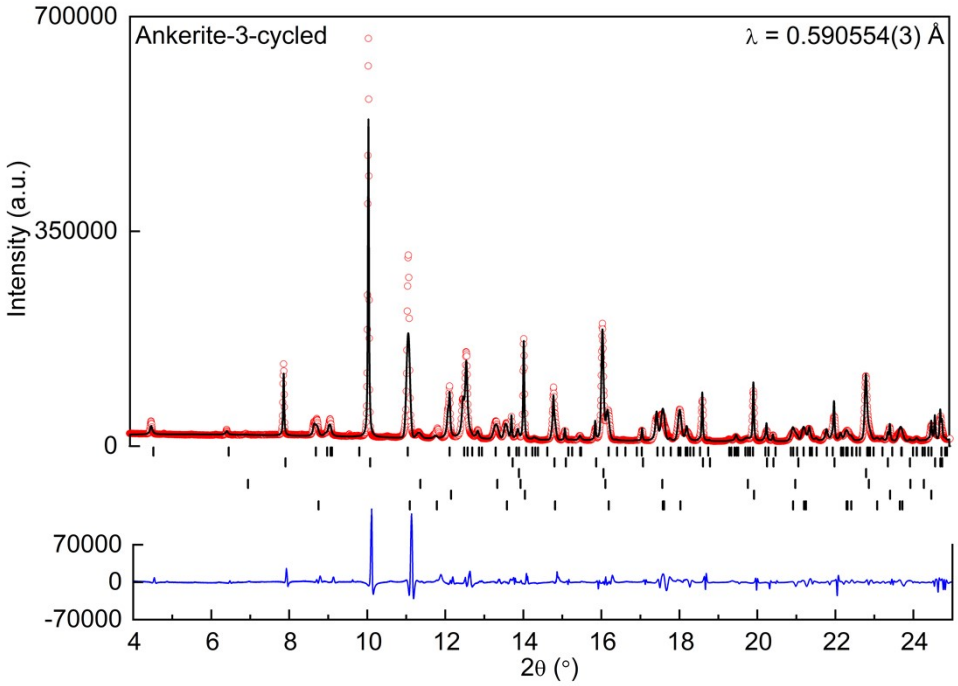

Figure S11. XRD pattern and fitting curve of the Rietveld refinement of cycled Ankerite-3. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, CaO, $MgFe_2O_4$, Quartz, and $Ca_2Fe_2O_5$ bottom to top, respectively.

Table S5. Quantitative composition analysis of the synthesised samples after the initial carbonation (heating up from room temperature to 750 °C at 5 bar CO_2).

Composition (%)	$CaCO_3$	$MgFe_2O_4$	MgO	$Ca_2Fe_2O_5$	Fe_2O_3
CC-N-1:1:1	48.0(2)	31.8(2)	15.7(2)	-	4.6(6)
BM-AC-1:1:1	39.1(1)	36.8(1)	15.4(1)	8.7(5)	-
CC-AC-1:1:1	46.8(1)	36.8(1)	16.4(2)	-	-
CC-AC-1:0.5:0.5	61.4(1)	26.3(1)	12.3(1)	-	-
CC-AC-1:0.3:0.3	68.2(5)	17.4(4)	10.0(3)	4.4(3)	-
CC-N-1:1	43.5(2)	-	-	-	56.6(2)

Table S6. Quantitative composition analysis of the synthesised samples in the carbonated state after 100 cycles at 750 °C (1 h vacuum desorption / 1 h absorption at 5 bar CO_2).

Composition (%)	$CaCO_3$	$MgFe_2O_4$	MgO	$Ca_2Fe_2O_5$	Fe_2O_3	CaO	$CaFe_3O_5$	$CaFe_2O_4$
CC-N-1:1:1	39.9(1)	34.9(1)	14.0(1)	11.1(7)	-	-	-	-
BM-AC-1:1:1	45.9(1)	31.9(9)	17.0(1)	5.2(6)	-	-	-	-
CC-AC-1:1:1	40.5(3)	36.4(3)	17.3(2)	5.9(2)	-	-	-	-
CC-AC-1:0.5:0.5	35.6(9)	-	16.3(8)	43.1(9)	-	2.3(2)	2.7(7)	-
CC-AC-1:0.3:0.3	27.9(3)	-	15.4(3)	40.0(3)	-	16.7(2)	-	-
CC-N-1:1	13.8(3)	-	-	-	11.4(5)	-	-	74.7(5)

XRD patterns of the synthesised Ca-Mg-Fe samples in the carbonated state before cycling (Figures S12-14-16-18-20-22) and in the carbonated state after 100 cycles at 750 °C with 1 hour vacuum desorption and 1 hour absorption at 5 bar CO_2 (Figures S13-15-17-19-21-23):

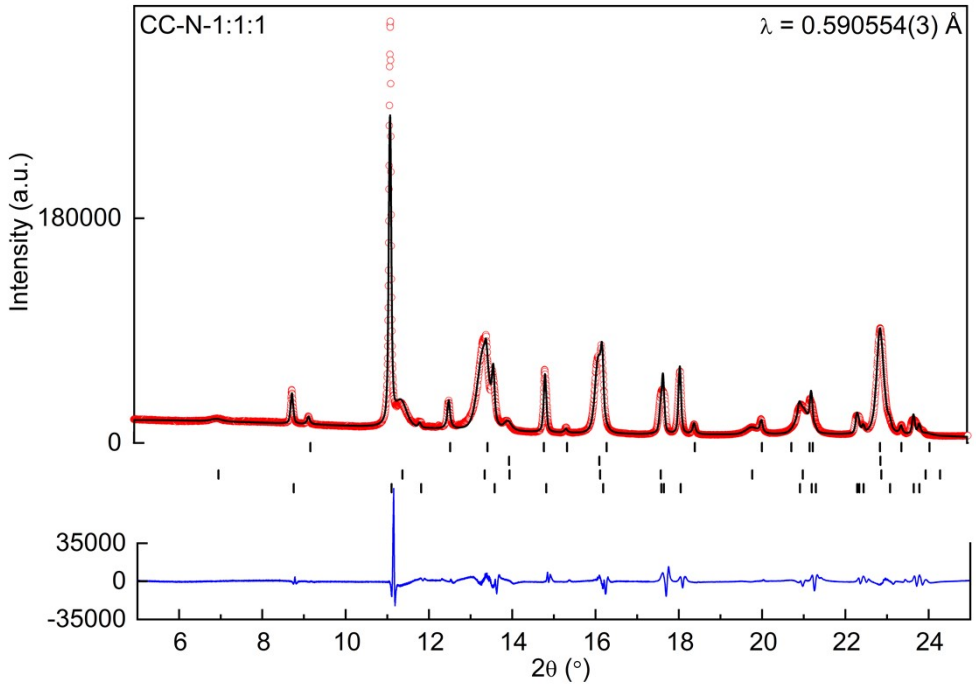

Figure S12. XRD pattern and fitting curve of the Rietveld refinement of CC-N-1:1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $MgFe_2O_4$, MgO and Fe_2O_3 bottom to top, respectively.

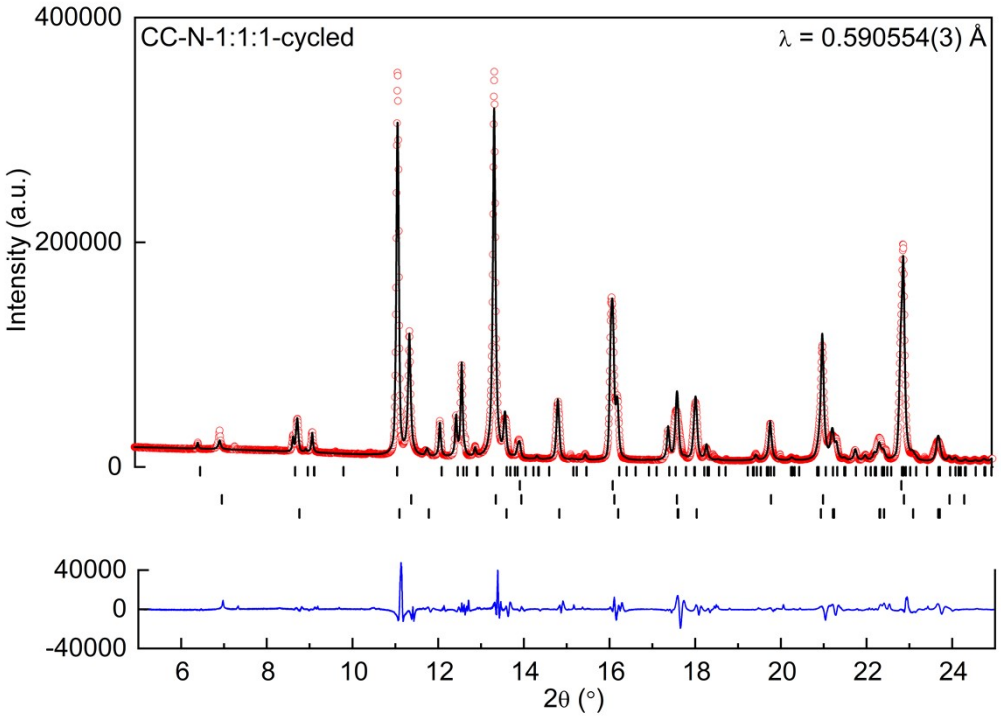

Figure S13. XRD pattern and fitting curve of the Rietveld refinement of cycled CC-N-1:1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $MgFe_2O_4$, MgO and $Ca_2Fe_2O_5$ bottom to top, respectively.

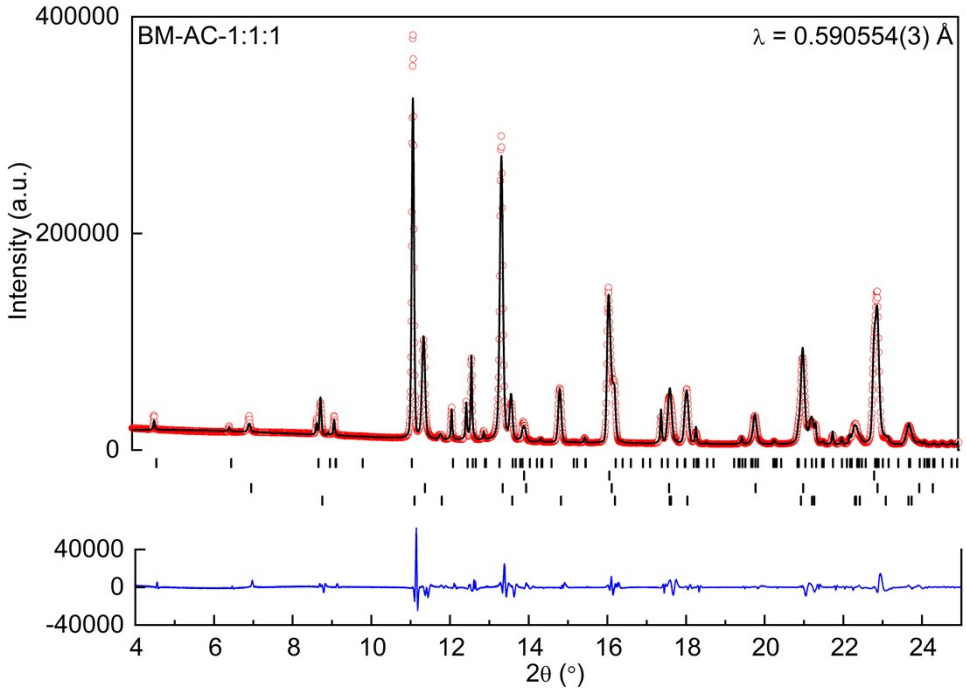

Figure S14. XRD pattern and fitting curve of the Rietveld refinement of BM-AC-1:1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $MgFe_2O_4$, MgO and $Ca_2Fe_2O_5$ bottom to top, respectively.

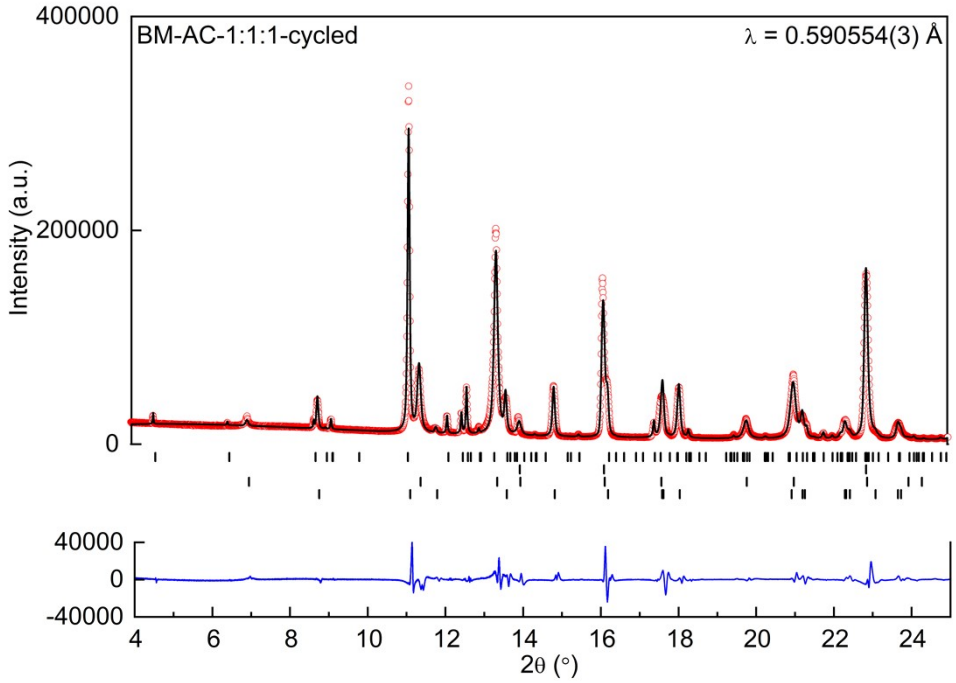

Figure S15. XRD pattern and fitting curve of the Rietveld refinement of cycled BM-AC-1:1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $MgFe_2O_4$, MgO and $Ca_2Fe_2O_5$ bottom to top, respectively.

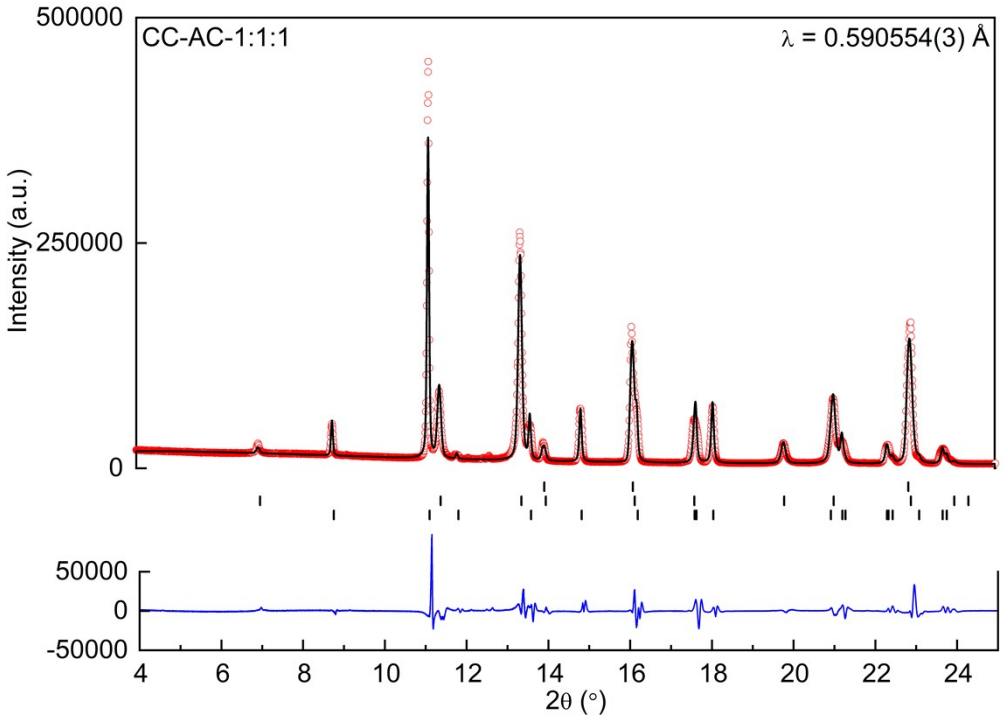

Figure S16. XRD pattern and fitting curve of the Rietveld refinement of CC-AC-1:1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $MgFe_2O_4$ and MgO bottom to top, respectively.

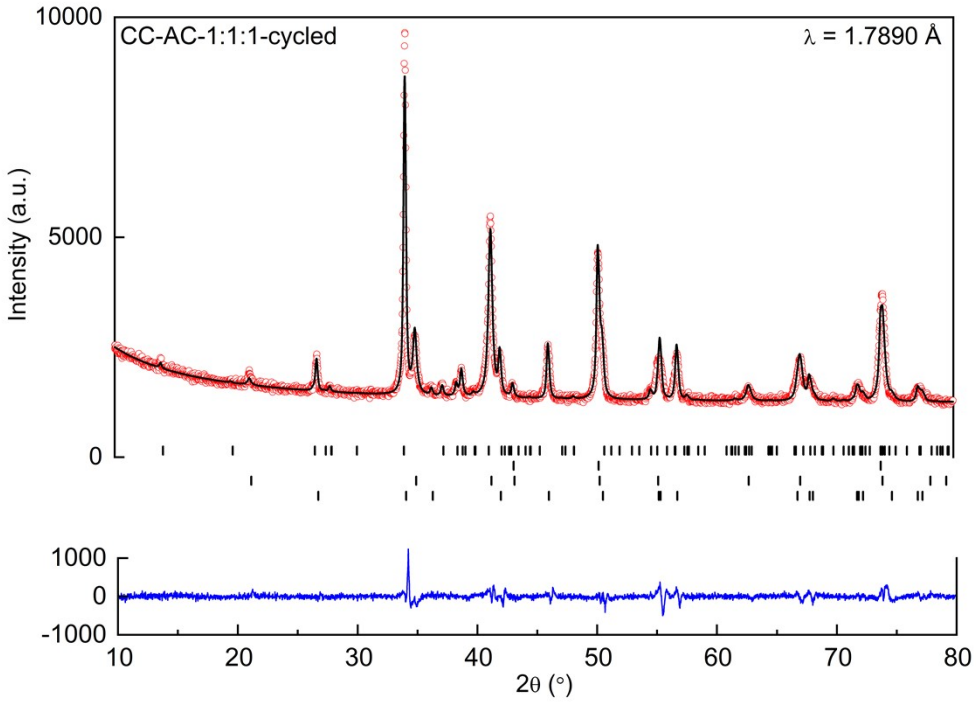

Figure S17. XRD pattern and fitting curve of the Rietveld refinement of cycled CC-AC-1:1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $MgFe_2O_4$, MgO and $Ca_2Fe_2O_5$ bottom to top, respectively.

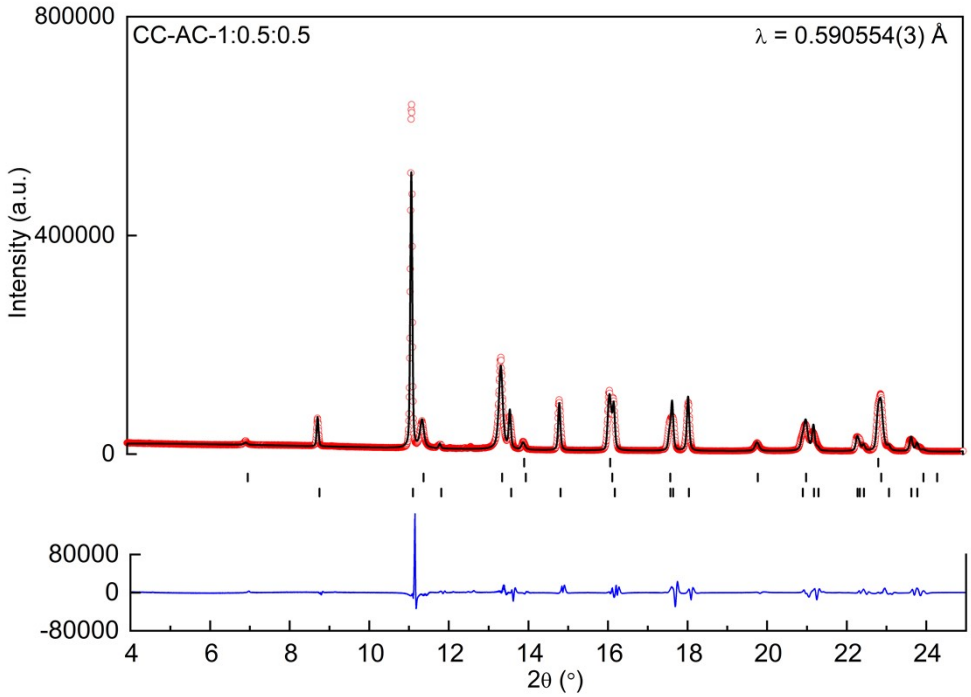

Figure S18. XRD pattern and fitting curve of the Rietveld refinement of CC-AC-1:0.5:0.5. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $MgFe_2O_4$ and MgO bottom to top, respectively.

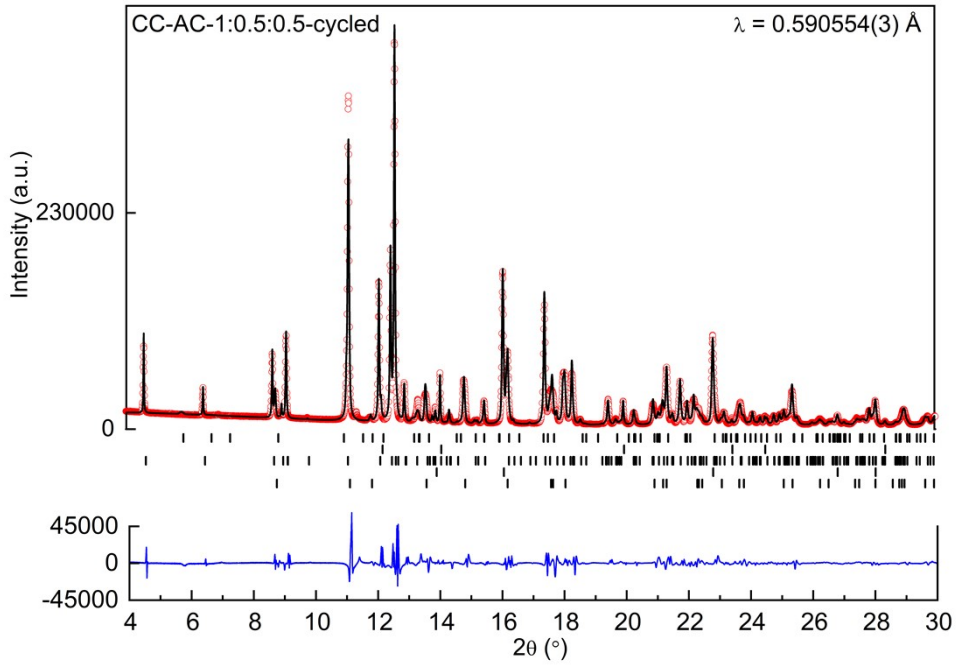

Figure S19. XRD pattern and fitting curve of the Rietveld refinement of cycled CC-AC-1:0.5:0.5. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, MgO, $Ca_2Fe_2O_5$, CaO and $CaFe_3O_5$ bottom to top, respectively.

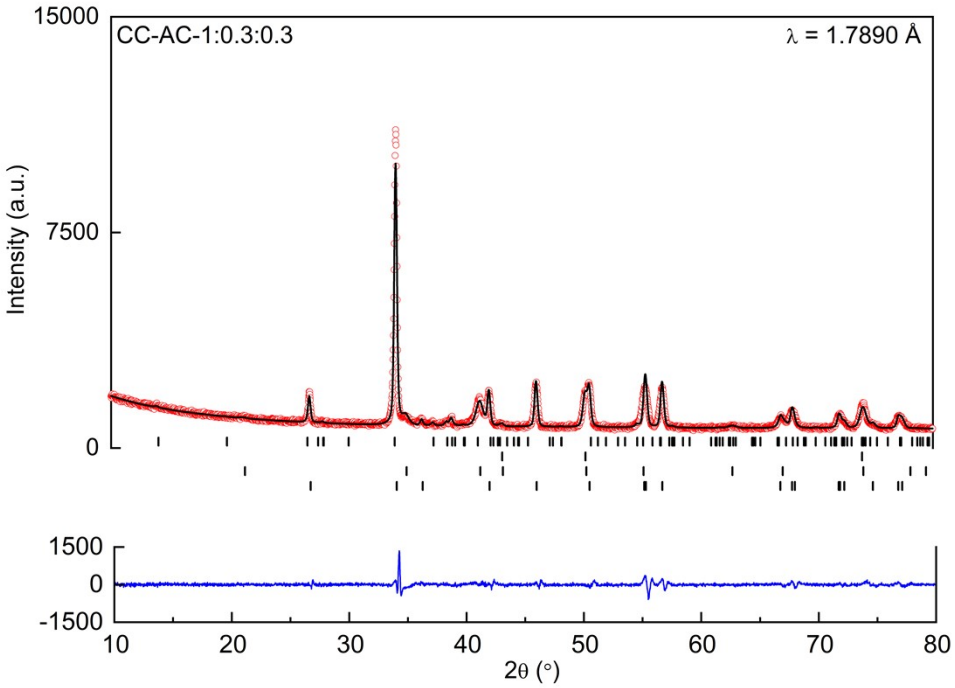

Figure S20. XRD pattern and fitting curve of the Rietveld refinement of CC-AC-1:0.3:0.3. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $MgFe_2O_4$, MgO and $Ca_2Fe_2O_5$ bottom to top, respectively.

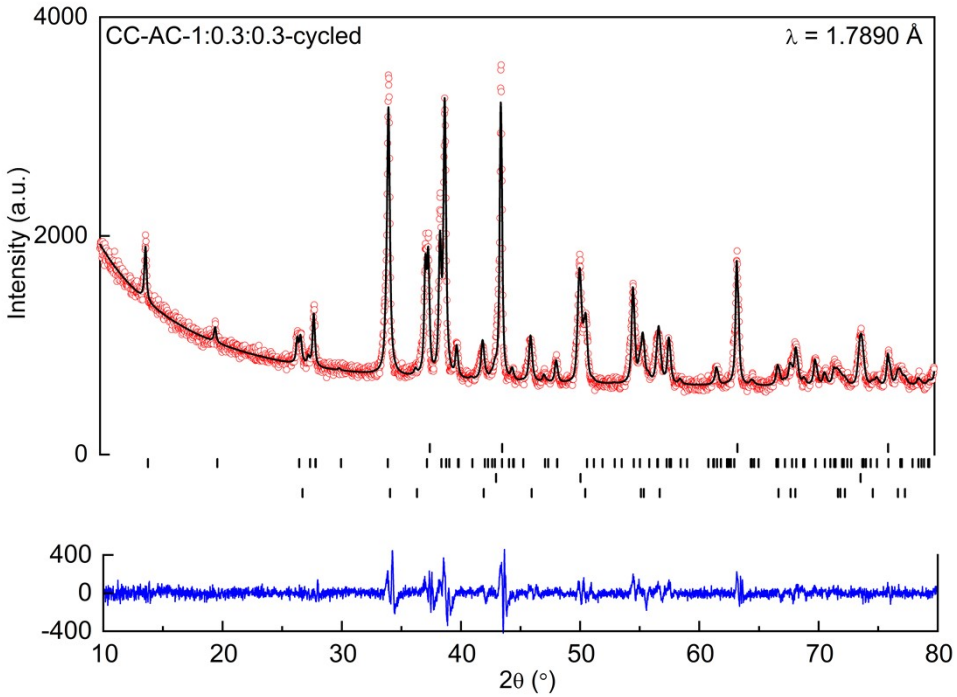

Figure S21. XRD pattern and fitting curve of the Rietveld refinement of cycled CC-AC-1:0.3:0.3. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, MgO, $Ca_2Fe_2O_5$, and CaO bottom to top, respectively.

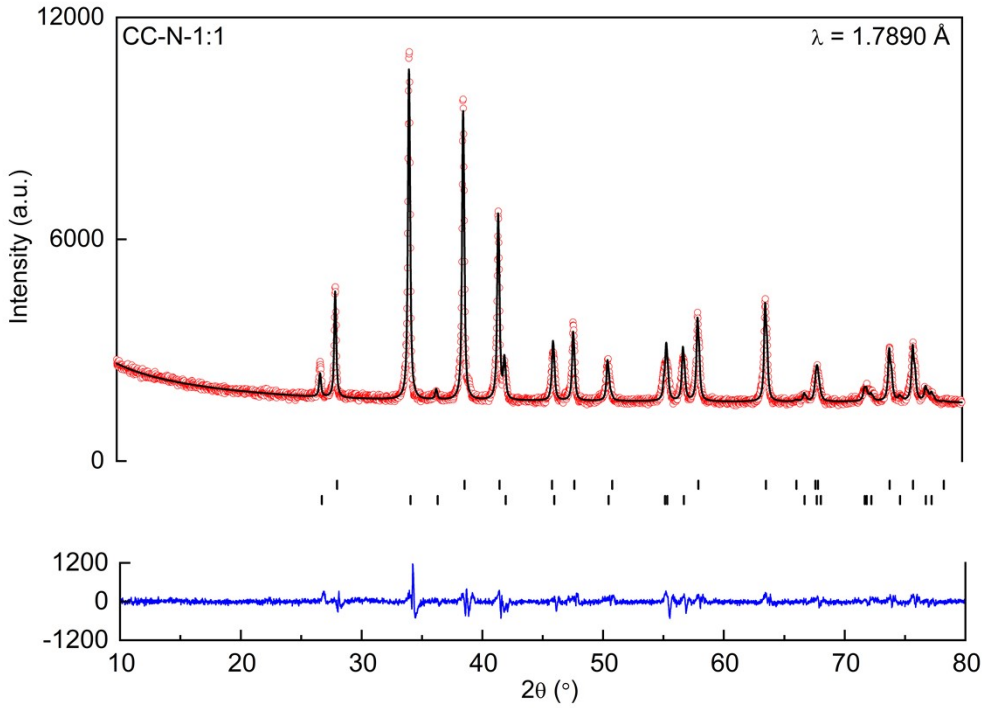

Figure S22. XRD pattern and fitting curve of the Rietveld refinement of CC-N-1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$ and Fe_2O_3 bottom to top, respectively.

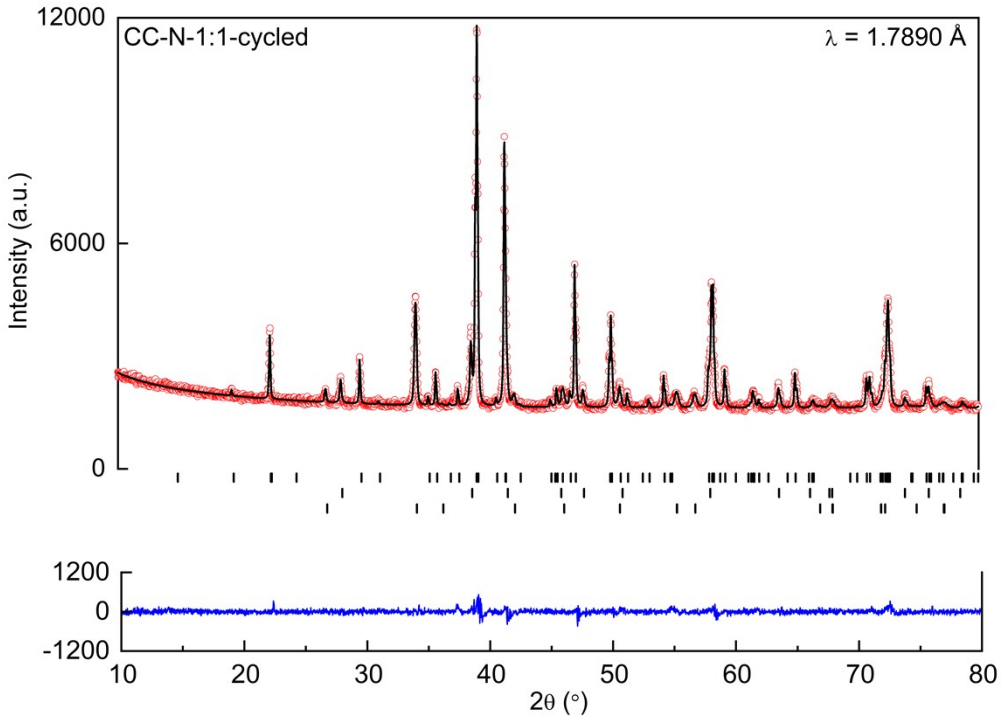

Figure S23. XRD pattern and fitting curve of the Rietveld refinement of cycled CC-N-1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, Fe_2O_3 and $CaFe_2O_4$ bottom to top, respectively.

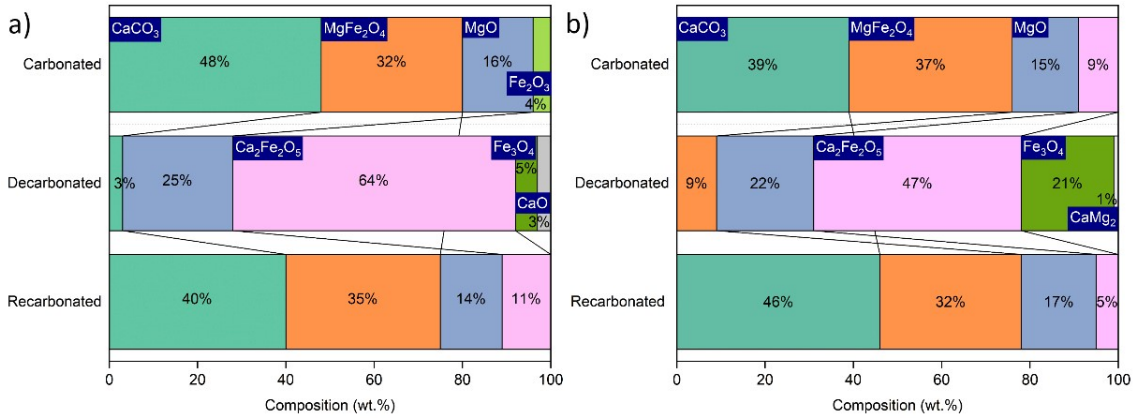

Figure S24. Composition of (a) CC-N-1:1:1 and (b) BM-AC-1:1:1, in the initial carbonated state, decarbonated and recarbonated at the end of the 100 cycles at 750 °C with 1 h vacuum desorption and 1 h absorption at 5 bar CO_2.

SR-XRD patterns of the synthesised samples with a Ca-Mg-Fe ratio of 1:1:1 in the decarbonated state after the 100 cycles of 1 hour vacuum desorption and 1 hour absorption at 5 bar CO_2 at 750 °C:

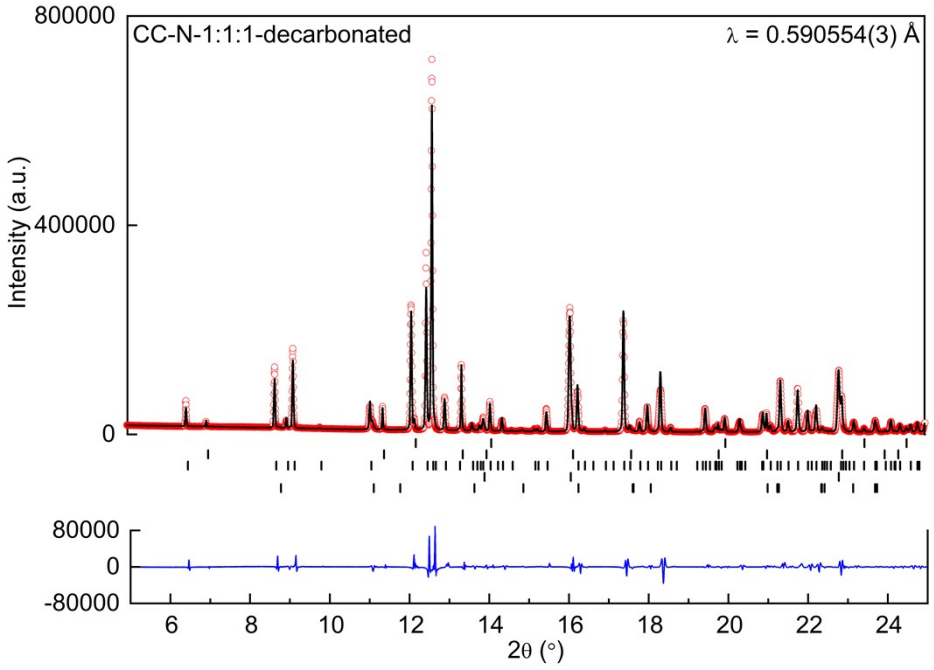

Figure S25. XRD pattern and fitting curve of the Rietveld refinement of decarbonated CC-N-1:1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, MgO, $Ca_2Fe_2O_5$, Fe_3O_4 and CaO bottom to top, respectively.

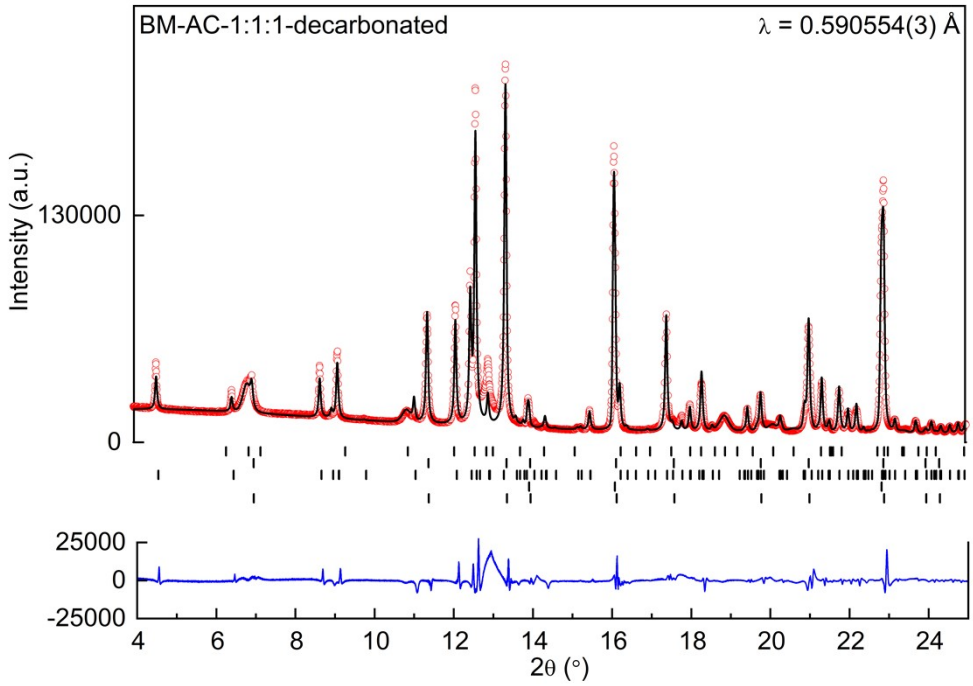

Figure S26. XRD pattern and fitting curve of the Rietveld refinement of decarbonated BM-AC-1:1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $MgFe_2O_4$, MgO, $Ca_2Fe_2O_5$, Fe_3O_4 and $CaMg_2$ bottom to top, respectively.

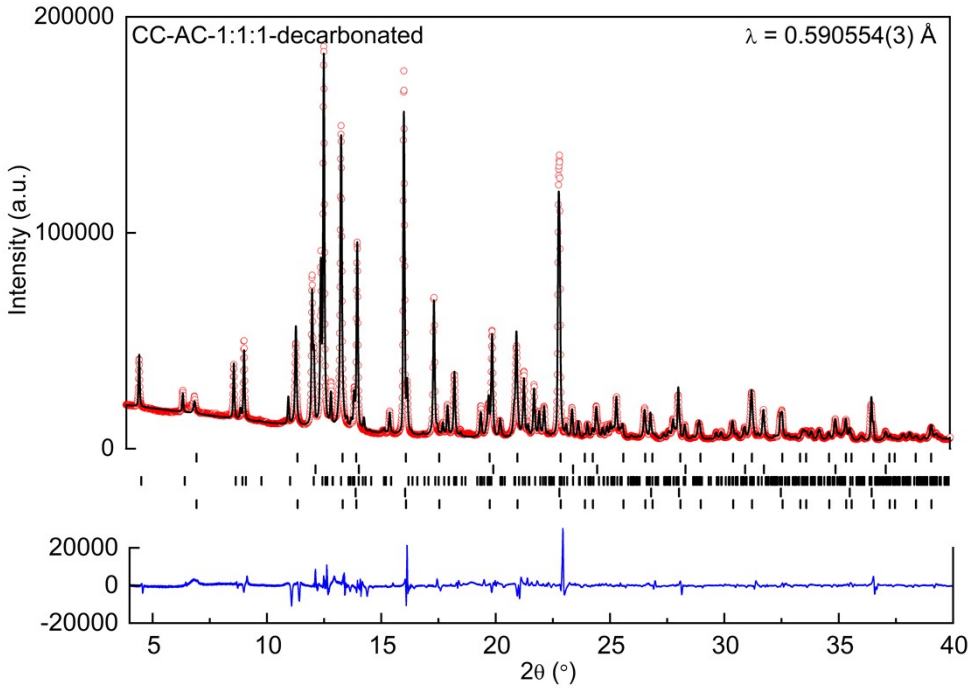

Figure S27. XRD pattern and fitting curve of the Rietveld refinement of decarbonated CC-AC-1:1:1. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $MgFe_2O_4$, MgO, $Ca_2Fe_2O_5$, CaO and Fe_3O_4 bottom to top, respectively.

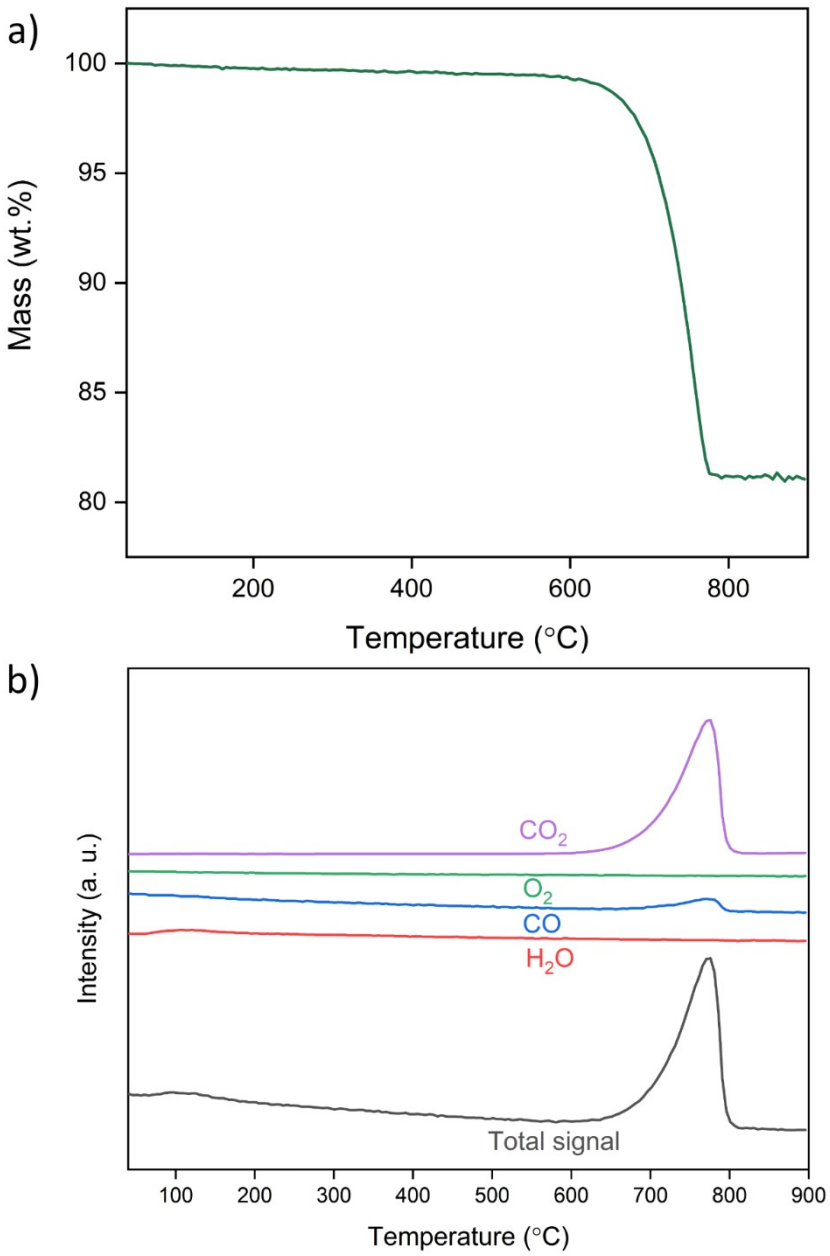

Figure S28. (a) TGA curve and (b) QMS data collected during the desorption while heating up to 900 °C at 20 K.min^{-1} under an Ar flow of 20 mL.min^{-1}.

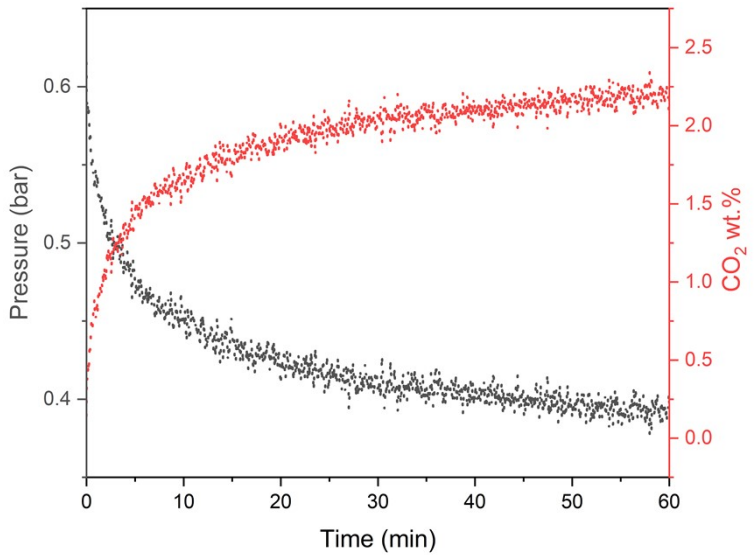

Figure S29. Low pressure (< 1 bar CO_2) absorption at 820 °C of a Ca:Mg:Fe (1:1:1) sample in the decarbonated state, after desorption PCI at 880 °C.

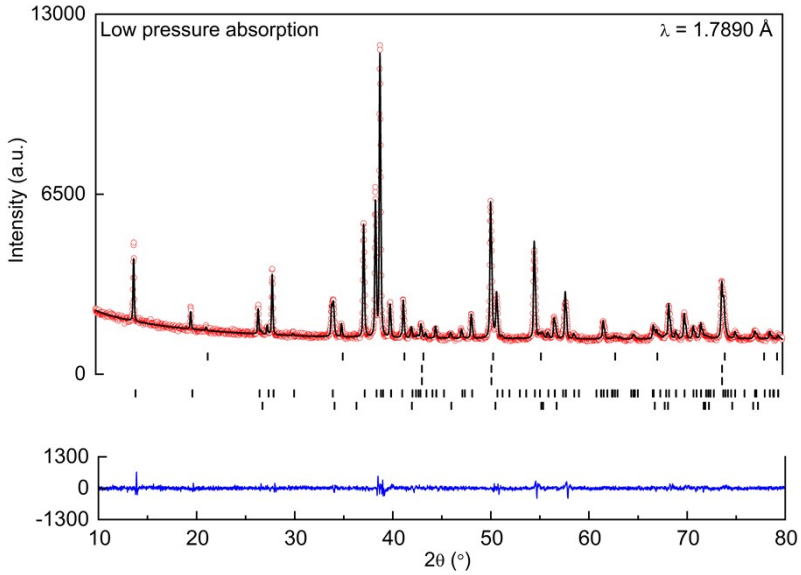

Figure S30. XRD pattern and fitting curve of the Rietveld refinement of CC-N-1:1 after low pressure (< 1 bar CO_2) absorption 820 °C for 1 h. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $Ca_2Fe_2O_5$, MgO, Fe_3O_4 and $MgFe_2O_4$ bottom to top, respectively.

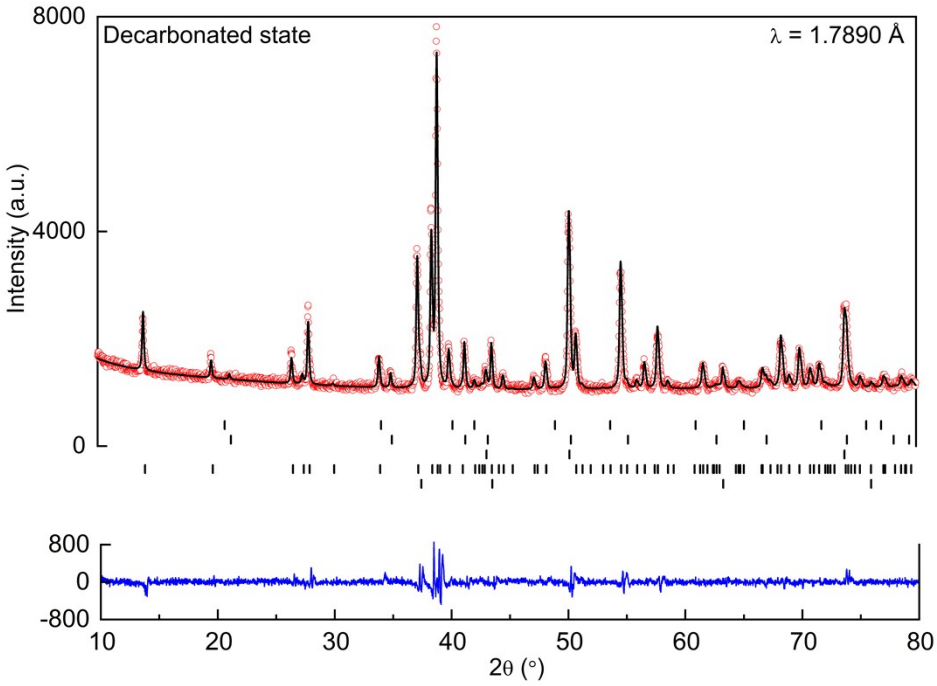

Figure S31. XRD pattern and fitting curve of the Rietveld refinement of CC-N-1:1 fully decarbonated at the end of the desorption PCI measurement at 880 °C. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$, $Ca_2Fe_2O_5$, MgO, Fe_3O_4 and $MgFe_2O_4$ bottom to top, respectively.