minerals

MDPI

Supplementary

S1: Rietveld Refinements

The fundamental parameters approach as implemented in TOPAS is applied for the refinements of X-ray powder data. Parameters of the measurement and the refinement are summarized in chapter 2.3. and Table S1.

Table S1. Parameters for XRD measurement and Rietveld refinement.

Instrumental and Refinement Variables	Settings and Parameters
Goniometer radius	240 mm
Fixed divergence slit angle	0.125°
Antiscattering slit angle	0.5°
Sample spinning	1 s
Antiscattering slit angle refracted beam	7.5°
Background	Chebychev polynomial 4th order, 1/X Bkg
Detector	Linear PSD
2Th angular range	3.347° 2θ
Source length	12 mm
RS length	14 mm
Prim./Sec. Soller	0.04 rad (2.3°)
LP factor	0
Zero error	refined from measurement of silicon standard [37]: −0.001946
sample displacement and sample length:	refined for each measurement

Corundum (Al_2O_3 α-phase, Alfa Aesar, 99.95%) is used as an internal standard in XRD measurements. Lattice parameters, atomic positions, and isotropic thermal parameters of the corundum powder were refined in a measurement with 10 wt% of the standard reference material CeO_2 (NIST 674b, Cerac Inc., Milwaukee, WI). The CIF file of CeO_2 674b determined by Argonne National Laboratory was used for the refinement. The lattice parameter of CeO_2 was fixed at 5.11153 Å according to the value given in the NIST certificate of analysis [38]. Isotropic temperature factors of Ce and O were calculated from the U_{iso} values determined by Marchbank et al. [39] according to:

$$B_{eq} = U_{iso} \cdot 8 \cdot \pi^2$$

The resulting values of B_{eq} = 0.26 for Ce and 0.44 for O were fixed during the refinements. The diffractogram shows no sign of an additional crystalline phase. As the mass absorption coefficient of Ce is very high (301 cm^2/g) microabsorption has to be taken into account [40] by including the Brindley correction in the refinement. The particle radius of corundum was set to 0.25 µm according to the manufacturer data (0.25–0.45 µm). As the mass absorption coefficient of corundum is only 32 cm^2/g the impact of small differences in particle size is small. However, for CeO_2 the impact of microabsorption on the phase contents is significant. According to the NIST Certificate, a phase purity of 91.36 % is expected, whereas the study of Marchbank et al. [39] evidenced a lower amorphous content of 4.8 %. By assuming an amorphous content of 0.48 wt% in the sample, the particle radius of CeO_2 has to be 3.4 µm instead of 0.5 µm which was determined in Pederson et al. [40]. The lowering of the particle size results in negative amorphous contents. As this particle radius is much higher than the expected value, corundum is assumed to be completely crystalline. The refined lattice parameters for corundum are a = 4.75996 and c = 12.99396 Å. Only minor differences to the cif file were found in the atomic positions (Al: 0 0 0.35165, O: 0.30813 0 0). The temperature factors are 0.65 for Al and 0.66 for O.

The structural models used in the refinements are listed with their literature references in Table S2. All temperature factors included in the literature data were used for the refinements (except ye'elimite). If only U is given these values were transformed into Beq

according to the equation above. Beq factors were set to 1 if neither B nor U are included in the literature data. Atomic positions and Beq factors were not refined. Lattice parameters were refined in the range of ±0.05 for all phases. Larger deviations were allowed only in individual cases after visual inspection. Due to the strong overlap of C_2S peaks, the lattice parameters of α'H-C_2S were refined only once for the samples synthesized at 800 °C, respectively. In all other refinements, the lattice parameters of α'H-C_2S were fixed to these values to avoid overestimation due to the strong overlap with β-C_2S.

Table S2. Structure models and their parameters used for the Rietveld refinement. MD-March Dollase, sh-spherical harmonics. Column Data shows the radiation type and sample used for data collection (sc-single crystal, pow-powder, X-X-ray, Sy-synchrotron, N-neutron).

Phase	Space Group	References	Data	Orientation
Raw materials				
α-Quartz	*P3$_2$21*	Le Page et al. 1976 [41]	scX	no
Calcite	*R-3cH*	Liu et al. 2014 [42]	powX	>10 wt% MD104
11Å Tobermorite	*B11m*	Merlino et al. 2001 [43]	scX	MD020, 002
Aragonite	*Pmcn*	De Villiers 1971 [44]	scX	no
Vaterite	*P6$_3$/mmc*	Kamhi 1961 [45]	scX	no
Anhydrite	*Amma*	Hawthorne et al. 1975 [46]	scX	no
Bassanite	*I121*	Ballirano et al. 2001 [47]	powX	no
Microcline	*C-1*	Allan et al. 1997 [48]	scX	MD001
Albite	*C-1*	Winter et al. 1979 [49]	scX	MD001
Sinjarite	*Pbcn*	Leclaire et al. 1977 [50]	scX	no
Calcination product				
α'H-C_2S	*Pnma*	Mumme et.al 1995 [51]	powSy	no
β-C_2S	*P12$_1$/n1*	Mumme et al. 1995 [51]	powSy	>20 wt% MD100+010
γ-C_2S	*Pbnm*	Mumme et al. 1996 [52]	powN	no
Ellestadite	*P6$_3$/m*	Fang et al. 2014 [28]	powN	>8 wt% sh4
Mayenite	*I-43d*	Galuskin et al. 2012 [53]	scX	no
Rusinovite	*Cmcm*	Galuskin et al. 2011 [34]	scX	no
Rondorfite	*Fd-3m*	Ye Ruilun 1987 [54]	scX	no
$CaCl_2$	*Pbcn*	Anselment 1985 [55]	scX	no
$Ca_2SiO_3Cl_2$	*I4*	Golovastikov et al. 1977 [56]	-	no
Ternesite	*Pnma*	Irran et al. 1997 [57]	scX	>10 wt% sh4
Lime	*Fm-3m*	Huang et al. 1994 [58]	powN	no
Wollastonite	*P12$_1$/a1*	Hesse 1984 [59]	scX	no
Melilite	*P-42$_1$m*	Merlini 2008 [60]	scX	no
Spurrite	*P12$_1$/a1*	Grice 2005 [61]	scX	>10 wt% sh4
Brownmillerite	*Ibm2*	Colville et al. 1971 [62]	scX	no
Ye'elimite	*I-43m*	Cuesta et al. 2014 [63]	powSy	no
Portlandite	*P-3m1*	Desgranges et al. 1993 [64]	scN	no
Merwinite	*P12$_1$/a1*	Moore et al. 1972 [65]	scX	no
Rankinite	*P21/a*	Kusachi et al. 1975 [66]	scX	no
Bredigite	*P2nn*	Moore et al. 1976 [67]	scX	no

* OH^- substituted by Cl^-.

S2: Calculation of the composition of the amorphous content

For the calculation of the composition of the amorphous content (Table S3), the H_2O, CO_2, and SO_3 contents determined from the weight losses in the thermal analysis were used (temperature ranges 30–500 °C, 500–900 °C, and 900–1400 °C). The chlorine content (combustion IC) was subtracted from the amount of SO_3. All other oxide contents determined by XRF and chlorine measured by combustion IC were normalized to a sum of 100 with the data from thermal analysis (raw data in Table S4). The sums of oxide contents in the crystalline phases (Table S5) were calculated and subtracted from these values. Table 5 summarizes the compositions of the amorphous contents for the raw mixtures and the samples heated to 700–1200 °C. The difference between the sum of all amorphous oxides and the amorphous content determined by XRD ranges between 0.1 and −0.6 wt% for all datasets. The oxide contents in the amorphous part were ascribed to mineral compositions according to the crystalline phases determined in the sample. Chlorine was calculated as $CaCl_2$, CO_2 as $CaCO_3$, and SO_3 as $CaSO_4$. In the high-temperature samples, Fe_2O_3 was ascribed to low-crystalline brownmillerite. As minor amounts of feldspars were found in the raw materials, Al_2O_3 was calculated as $CaAl_2Si_2O_8$ in the raw mixtures. The residual amounts of $MgO+Al_2O_3+Fe_2O_3$ were below 1.0 wt% for most of the samples. Only in the low-temperature data of sample P the residuals that could not be ascribed to phase compositions sum up for higher amounts to the extent of 1.6 wt%. The C/S ratio was calculated for the residual amorphous content. It is ≤2 in all high-temperature samples and <1 in the raw mixtures. Due to the low C/S-ratios C_2S in the amorphous content for all other high-temperature samples was calculated according to the residual amount of CaO and the existence of amorphous SiO_2 was assumed.

Table S3. Composition of the amorphous content in samples D2, P, and D1 heated to different temperatures. Diff.= sum of amorphous oxides-amorphous content XRD, Res = residue of amorphous oxides $MgO + Al_2O_3 + Fe_2O_3$ after subtraction of Al_2O_3 and Fe_2O_3 in amorphous brownmillerite and feldspar, C/S-ratio = molar ratio CaO/SiO_2 in amorphous content after subtraction of CaO in amorphous $CaCl_2$, $CaCO_3$, $CaSO_4$, brownmillerite, and feldspar, $C_2S_{total} = C_2S_{crystalline}+C_2S_{amorphous}$.

Sample	H_2O	CO_2	SO_3	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	Cl^-	Diff.	Res	C/S-ratio	C_2S_{amorph}	C_2S_{total}
D2														
25	3.4	2.2	2.7	10.3	11.8	0.5	1.2	0.4	0.9	-0.2	0.9	0.4	-	-
800	0.4	2.8	0.7	8.0	5.4	0.4	0.8	0.1	-0.4	-0.3	0.2	0.7	5.4	13.8
900	0.5	0.6	1.2	3.0	5.0	0.3	0.3	0.0	-0.8	-0.6	-0.2	0.2	1.7	27.4
950	0.5	0.8	1.8	6.7	6.4	0.4	0.0	0.3	-0.6	-0.4	-0.5	0.7	6.2	50.0
1000	0.5	0.6	0.1	7.3	4.6	0.3	0.2	0.5	-0.2	-0.5	0.0	1.4	9.5	57.5
1050	0.3	0.4	0.7	6.8	3.6	0.2	0.0	0.4	-0.2	-0.3	0.1	1.7	8.7	56.6
1100	0.2	0.2	0.7	8.1	6.3	0.5	0.3	0.1	-0.2	-0.5	-0.5	1.2	10.4	54.1
P														
25	3.2	2.0	0.9	15.0	14.5	0.7	1.6	0.6	0.8	0.0	1.3	0.9	-	-
700	0.5	3.2	0.1	12.0	9.1	0.3	1.4	0.6	0.4	-0.1	1.6	0.9	11.2	21.4
800	0.6	1.9	0.3	7.2	4.7	0.7	0.8	0.5	0.4	-0.3	0.1	0.8	5.6	18.0
900	0.7	1.3	0.5	8.4	4.8	0.7	0.6	0.6	0.4	-0.1	-0.1	1.2	8.4	56.9
1000	0.3	0.8	0.7	7.0	4.2	0.6	0.3	0.7	0.2	-0.1	0.0	1.2	7.2	71.0
1100	0.4	0.5	0.6	8.4	4.9	0.8	0.3	0.3	0.0	-0.2	-0.	1.4	10.2	65.3
1200	0.2	0.3	0.7	17.6	8.3	0.9	1.9	-0.3	-0.3	-0.3	0.11	2.0	24.3	66.5
D1														
25	4.4	2.7	0.3	9.3	10.6	0.4	1.0	0.3	0.9	-0.1	0.8	0.5	-	-
700	0.6	2.4	-0.3	7.0	5.8	0.3	0.8	0.3	0.7	0.0	0.5	0.6	5.3	11.5
800	1.3	1.8	0.0	6.0	4.5	0.4	0.3	0.2	0.8	0.1	-0.3	0.7	4.4	10.7
900	0.4	1.3	0.7	6.4	4.1	0.4	0.2	0.3	0.8	0.1	-0.3	0.9	5.1	53.0
1000	0.3	0.6	0.7	9.9	5.3	0.4	0.2	0.2	0.6	-0.3	-0.2	1.6	12.2	79.9
1100	0.4	0.3	0.6	9.3	5.4	0.5	0.2	0.0	0.1	-0.2	-0.7	1.6	12.1	76.2
1200	0.1	0.1	0.9	16.7	8.1	0.6	1.4	-0.2	-0.4	-0.2	0.2	2.0	23.5	79.6

Table S4. Raw data: Loss of ignition and oxide contents determined by RFA, chlorine contents determined by combustion IC and H_2O, CO_2, and SO_3+Cl determined by thermal analysis. Contents of Na_2O, K_2O, and TiO_2 are <0.2 wt%.

Name	LoI	MgO	Al_2O_3	SiO_2	SO_3	CaO	Fe_2O_3	Cl^-	H_2O(TG)	CO_2(TG)	SO_3+Cl(TG)	C/S-ratio
D2_800	14.72	0.44	1.43	26.51	5.64	49.20	0.57	1.29	0.39	13.45	7.69	1.99
D2_900	6.28	0.49	1.60	29.27	6.26	54.03	0.63	1.39	0.50	4.87	8.81	1.98
D2_950	1.89	0.51	1.63	30.55	6.49	56.20	0.65	1.40	0.51	0.90	8.96	1.97
D2_1000	1.40	0.51	1.67	30.82	6.60	56.91	0.66	1.35	0.45	0.65	7.13	1.98
D2_1050	1.23	0.52	1.66	30.73	6.64	57.21	0.66	1.29	0.26	0.52	7.80	1.99
D2_1100	1.05	0.51	1.69	30.93	6.64	57.30	0.66	1.21	0.15	0.31	7.81	1.98
P_700	17.32	0.68	1.83	26.70	2.35	49.00	0.79	1.28	0.46	16.82	3.83	1.97
P_800	10.91	0.73	1.99	28.60	2.54	52.70	0.84	1.34	0.57	10.13	4.03	1.97
P_900	2.38	0.80	2.16	31.30	2.79	57.60	0.92	1.40	0.72	2.34	4.31	1.97
P_1000	1.23	0.82	2.22	32.00	2.82	58.80	0.94	1.29	0.31	0.90	4.54	1.97
P_1100	0.55	0.83	2.27	32.10	2.82	58.80	0.94	1.09	0.40	0.50	4.15	1.96
P_1200	0.47	0.83	2.25	32.20	2.38	59.10	0.95	0.52	0.20	0.32	3.37	1.97
D1_700	21.46	0.40	1.21	26.20	0.70	48.20	0.49	1.22	0.57	20.5	1.97	1.97
D1_800	12.52	0.44	1.41	29.30	0.79	53.80	0.56	1.43	1.30	11.48	2.35	1.97
D1_900	4.16	0.48	1.50	32.20	0.86	59.10	0.61	1.42	0.37	3.82	3.00	1.97
D1_1000	1.07	0.50	1.54	33.20	0.88	60.90	0.63	1.34	0.25	0.62	2.61	1.97
D1_1100	0.71	0.50	1.56	33.40	0.82	61.20	0.63	0.97	0.35	0.39	2.30	1.96
D1_1200	0.25	0.51	1.55	33.40	0.62	61.30	0.63	0.40	0.10	0.17	1.82	1.97

Table S5. Raw data: Phase contents determined by XRD and Rietveld refinement. E.s.d.s of the refinement are given in parentheses. Additional phase contents are ≤1.5 wt%: brownmillerite; ≤1 wt%: $CaCl_2$, albite, and microcline; <0.5 wt%: $Ca_2SiO_3Cl_2$ and ye'elimite.

Name	amorphous	β-C_2S	αH-C_2S	γ-C_2S	Quartz	$CaCO_3$	Lime	Anhydrite	Ellestadite	Chlormayenite	Rusinovite	Ternesite	Spurrite	Rankinit	Melilite	Bredigite	Merwinite	Wollastonite	Rondorfite	GoF	DW
D2_800	18.7(9)	1.7(2)	6.7(2)	0.53(9)	9.0(1)	21.3(2)	0.13(5)	0.58(6)	22.1(2)	0.84(8)	0.8(1)	1.0(2)	12.9(2)		0.6(1)		1.9(2)	0.31(7)	0.18(6)	2.10	0.32
D2_900	11(1)	23.5(4)	2.2(2)	1.1(2)	4.3(4)	6.4(1)	1.96(5)	0.6(1)	23.2(3)	2.3(1)	0.3(1)	2.4(3)	15.2(3)		1.4(2)		1.6(2)	0.5(1)	0.6(1)	2.56	0.27
D2_950	16(1)	43.5(4)	0.4(1)	0.4(1)	2.8(3)	0.16(5)	4.05(5)	0.69(6)	21.1(2)	2.95(9)		2.6(2)	0.5(2)		0.9(1)		0.8(2)	0.2(1)	0.2(1)	2.00	0.32
D2_1000	14.1(9)	48.0(3)		0.42(6)	3.81(5)		2.45(4)	0.66(5)	19.4(2)	2.60(7)	0.6(1)	4.7(1)	0.6(1)		0.08(5)		0.19(9)	0.5(1)	0.2(1)	1.74	0.43
D2_1050	12(1)	47.9(4)		0.6(1)	3.59(7)	0.17(7)	0.10(3)	0.60(6)	18.3(2)	3.26(8)	0.9(1)	7.5(2)	0.5(1)	0.6(2)	0.24(6)	1.0(1)	0.4(1)	0.5(1)		1.64	0.50
D2_1100	16.6(7)	43.7(3)		0.61(9)	0.99(5)		0.13(3)	0.41(6)	17.3(2)	2.81(6)	0.08(6)	10.2(2)	0.6(1)		1.1(1)	3.5(1)		1.1(1)		1.56	0.53
P_700	28(1)	3.0(2)	7.2(3)	2.0(2)	8.08(8)	29.0(2)	0.03(2)	1.15(8)	7.6(2)	0.65(9)			8.4(3)				0.3(1)	2.3(1)	0.7(1)	1.88	0.40
P_800	17.3(8)	3.0(2)	9.4(2)	1.8(2)	5.80(6)	11.7(1)		0.44(6)	8.7(2)	2.29(8)	1.0(1)	0.4(1)	31.5(3)		0.15(5)		1.8(2)	3.6(1)	0.26(6)	1.94	0.52
P_900	18.0(9)	46.2(4)	2.3(2)	1.0(1)	2.88(5)		0.69(3)	0.25(3)	9.4(2)	3.21(9)	0.9(1)	0.6(2)	10.9(2)		0.35(7)		1.5(2)	1.1(1)		1.53	0.49
P_1000	15.0(7)	63.8(4)		0.68(9)	2.11(4)		0.17(5)	0.43(6)	9.9(1)	3.90(9)	0.7(1)	0.12(7)	0.5(1)		0.06(5)		0.5(1)	0.6(1)	0.13(6)	1.67	0.46
P_1100	16.1(6)	55.1(4)		0.59(9)	1.38(5)		0.09(2)	0.25(3)	9.(1)	3.95(7)	0.30(9)	0.30(8)	0.5(1)		0.26(5)	7.3(1)	0.6(1)	2.0(1)		1.54	0.5
P_1200	29.5(5)	42.1(3)		0.68(8)	0.15(2)		0.15(3)	0.30(4)	8.3(1)	0.55(6)	0.77(8)	0.20(7)	0.27(9)	7.7(1)	7.08(9)	1.0(1)		0.11(3)		1.52	0.58
D1_700	17.6(1)	1.9(2)	4.3(2)	1.2(2)	11.1(1)	37.3(3)	0.05(3)	0.51(6)	2.5(2)	0.56(8)	1.3(1)	0.8(2)	17.3(3)				0.4(1)	0.8(1)	1.6(1)	1.89	0.44
D1_800	15.2(9)	2.3(2)	4.0(2)	1.4(2)	6.53(7)	10.9(1)		0.39(7)	2.4(2)	1.93(9)	0.26(9)	0.7(2)	48.9(4)				1.4(2)	0.9(1)	1.49(9)	1.84	0.39
D1_900	14.5(8)	46.9(3)	1.0(2)	0.56(7)	2.42(5)			0.43(6)	2.4(1)	2.65(8)	0.5(1)	0.4(1)	25.1(2)		0.21(6)		1.2(2)	0.18(5)	0.38(8)	1.68	0.53
D1_1000	18.2(9)	67.7(5)		1.1(1)	1.06(5)		0.07(2)	0.34(6)	1.5(1)	2.58(9)	1.8(1)	0.16(7)	0.3(1)				1.2(2)	0.4(1)	1.99(9)	2.03	0.4
D1_1100	17.0(7)	64.1(4)		0.9(1)	0.5(1)		0.13(3)	0.28(4)	2.1(1)	2.80(7)	4.3(1)	0.23(8)	0.8(1)	0.3(1)	0.8(1)	3.1(1)	1.2(1)	0.4(1)		1.82	0.47
D1_1200	27.4(6)	56.1(3)		0.5(1)			0.10(2)	0.41(5)	1.2(1)	0.23(7)	7.4(1)	0.14(6)	0.24(9)	0.5(1)	4.41(9)		0.20(9)	0.05(3)		1.69	0.56

S3: Calculation of the yield for CaO in C_2S and ellestadite

The amounts of crystalline and non-crystalline C_2S, as well as ellestadite, were normalized to the loss of ignition of the raw samples before high-temperature treatment. The yield was calculated from these values according to the equation given in the main part of the paper. The reasonability of these results was proven by the calculation of the yield of all other crystalline and non-crystalline phases and by the addition of these values to the yields of C_2S and ellestadite. All sums vary between 0.98 and 1.01, which proves the reasonability of the calculations.

Table S6. Calculation of the yield of the products C_2S and ellestadite and mass balance calculation for CaO in other crystalline and amorphous phases. Phase amounts C_2S_{cry}, C_2S_{tot} and ellestadite are normalized to the loss of ignition of the raw material, Yield Prod. = sum of the yields of these phases, Sum Other = sum of the yield of all other crystalline and amorphous phases, Sum Total = sum prod.+sum other.

Sample	C_2S_{cry}	C_2S_{tot}	Ellestadite	Yield C_2S_{cry}	Yield C_2S_{tot}	Yield Ellest.	Yield Prod.	Sum Other	Sum Total
D2									
800	7.13	11.67	18.77	0.11	0.18	0.24	0.42	0.57	1.00
900	19.86	21.19	17.93	0.31	0.33	0.23	0.56	0.43	0.99
950	32.31	36.88	15.58	0.50	0.57	0.20	0.78	0.21	0.99
1000	35.26	42.20	14.21	0.55	0.66	0.18	0.84	0.17	1.01
1050	35.13	41.50	13.43	0.55	0.65	0.17	0.82	0.18	1.00
1100	31.99	39.60	12.63	0.50	0.62	0.16	0.78	0.22	1.00
P									
700	9.16	19.25	6.84	0.13	0.28	0.08	0.37	0.61	0.98
800	10.34	15.03	7.24	0.15	0.22	0.09	0.31	0.67	0.98
900	36.89	43.31	7.15	0.54	0.64	0.09	0.72	0.26	0.98
1000	47.97	53.36	7.41	0.71	0.78	0.09	0.88	0.11	0.99
1100	41.14	48.78	7.32	0.61	0.72	0.09	0.81	0.18	0.99
1200	31.43	49.58	6.16	0.46	0.73	0.08	0.80	0.19	1.00
D1									
700	5.42	10.01	2.14	0.08	0.15	0.03	0.18	0.81	0.99
800	4.94	8.38	1.87	0.08	0.13	0.02	0.15	0.83	0.98
900	34.26	37.91	1.69	0.53	0.58	0.02	0.60	0.38	0.98
1000	46.94	55.37	1.04	0.72	0.85	0.01	0.86	0.12	0.98
1100	44.29	52.63	1.48	0.68	0.81	0.02	0.83	0.16	0.99
1200	38.58	54.75	0.82	0.59	0.84	0.01	0.85	0.14	1.00