Supporting information for the manuscript entitled;

Simultaneous ex-situ CO_2 mineral sequestration and H_2 production from New Caledonian mine tailings

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Gas phase data

S1.The composition of gas phase of MT1 experiment conducted at 473 K and 15 MPa.

MT1					
Duration	**H2**	**CH4**	**CO2**	**N2**	**O2**
(days)	**(µmols/g)**	**(µmols/g)**	**(mmols/g)**	**(mmols/g)**	**(mmols/g)**
0.1	4.54	-	94.6	0.24	0.04
0.9	1.44	-	94.0	3.84	0.99
1.8	1.35	-	91.0	7.98	2.02
2.8	4.76	-	106.8	-	-
5.8	6.62	-	113.8	0.24	0.04
7.8	5.94	-	119.1	-	-
8.8	8.42	-	127.0	-	-
9.8	8.01	0.17	130.9	-	-
13.0	0.21	-	136.4	-	-
13.8	6.11	0.24	143.0	-	-
16.0	16.92	0.23	149.3	-	-
20.0	15.20	0.27	154.1	-	-
22.8	17.87	-	159.8	-	-
23.8	19.99	-	165.9	0.05	-

S2. The composition of gas phase of MT2 experiment conducted at 523 K and 30 MPa.

MT2									
Duration	**H2**	**CH4**	**CO2**	**N2**	**O2**	**C2H6**	**C3H8**	**iC4H10**	**nC4H11**
(days)	**(µmols/g)**	**(µmols/g)**	**(mmols/g)**	**(mmols/g)**	**(mmols/g)**	**(µmols/g)**	**(µmols/g)**	**(µmols/g)**	**(µmols/g)**
0.00	0.00	0.00	179.13	0.13	0.02	-	-	-	-
0.69	0.00	0.43	184.38	0.18	-	-	-	-	-
0.96	0.00	5.71	189.23	0.18	-	-	-	-	-
1.71	0.00	0.44	195.42	0.18	-	-	-	-	-
1.96	3.48	0.21	200.97	-	-	-	-	-	-
4.68	2.79	0.22	206.68	0.17	0.19	-	-	-	-
5.88	5.64	0.65	211.31	0.29	0.03	-	-	-	-
6.68	7.67	1.44	215.93	0.61	0.11	-	-	-	-
7.72	6.52	0.76	228.60	0.46	0.04	-	-	-	-
8.92	8.37	0.75	228.11	0.23	-	-	-	-	-
11.71	43.67	4.82	231.46	0.24	-	0.41	0.59	0.04	1.27
13.71	47.75	12.33	228.82	6.52	1.46	4.01	1.93	0.36	2.23
14.71	37.48	3.59	242.22	0.25	-	-	0.38	0.03	0.72
18.71	53.80	2.56	247.42	0.40	0.04	-	0.42	-	0.67
20.75	117.57	5.94	253.49	0.64	0.09	-	0.58	0.03	0.99
22.75	58.49	1.41	258.83	-	-	-	-	-	-
25.76	76.69	2.00	263.83	-	-	-	-	-	-

S3.The composition of gas phase of MT4 experiment conducted at 573 K and 30 MPa.

MT4									
Duration	**H2**	**CH4**	**CO2**	**N2**	**O2**	**C2H6**	**C3H8**	**iC4H10**	**nC4H11**
(days)	**(μmols/g)**	**(μmols/g)**	**(mmols/g)**	**(mmols/g)**	**(mmols/g)**	**(μmols/g)**	**(μmols/g)**	**(μmols/g)**	**(μmols/g)**
0	0.00	0.10	183.56	0.38	0.10	-	-	-	-
0.76	116.17	9.93	146.34	0.78	0.15	-	0.82	-	1.89
1.13	106.77	11.32	147.27	4.92	1.14	-	1.95	0.09	2.89
1.80	0.00	0.47	200.07	2.47	0.47	-	-	-	-
2.85	186.29	26.19	138.04	22.60	-	3.70	10.72	0.60	11.08
4.04	0.00	1.76	208.04	3.71	0.93	-	-	-	-
6.83	145.06	1.73	219.28	-	-	-	-	-	-
8.83	283.50	1.22	226.74	-	-	-	-	-	-
9.88	35.97	8.47	230.83	1.40	0.17	0.79	2.12	0.10	2.87
13.83	73.78	5.85	238.71	0.20	0.02	-	0.45	0.04	1.40
15.88	41.76	4.72	245.09	0.15	0.01	-	0.37	0.30	0.73
17.88	48.17	5.49	249.76	0.16	0.01	-	-	0.19	0.71
20.88	21.94	1.88	245.44	-	-	-	-	-	-
24.01	41.18	24.14	247.30	0.50	0.12	8.16	16.95	0.74	14.76

S4. The composition of gas phase of MT2b experiment conducted at 523 K and 30 MPa. This is a blank experiment conducted at similar PT conditions in comparison with MT2, without introducing mine tailings in the reactor (due to technical difficulties, CO2 was not readjusted after the first sampling).

MT2b									
Duration (days)	**H2 (µmols/g)**	**CH4 (µmols/g)**	**CO2 (mmols/g)**	**N2 (mmols/g)**	**O2 (mmols/g)**	**C2H6 (µmols/g)**	**C3H8 (µmols/g)**	**iC4H10 (µmols/g)**	**nC4H11 (µmols/g)**
7.21	-	0.15	280.94	0.10	-	-	-	-	-
19.17	-	2.42	192.34	0.19	0.03	1.67	7.28	0.81	12.16
24.17	-	3.81	197.10	0.20	0.02	2.05	8.37	1.17	16.95

S5.The composition of gas phase of MT4b experiment conducted at 573 K and 30 MPa. This is a blank experiment without reactants in order to monitor H2 and CH4 concentrations. It was conducted at similar PT conditions in comparison with MT4, without introducing mine tailings in the reactor (due to technical difficulties, CO2 was not readjusted after the first sampling).

MT4b									
Duration (days)	**H2 (µmols/g)**	**CH4 (µmols/g)**	**CO2 (mmols/g)**	**N2 (mmols/g)**	**O2 (mmols/g)**	**C2H6 (µmols/g)**	**C3H8 (µmols/g)**	**iC4H10 (µmols/g)**	**nC4H11 (µmols/g)**
7.21	-	7.44	280.58	-	-	2.51	6.02	0.30	7.30
19.17	-	7.76	191.52	0.33	0.16	6.72	26.92	3.55	52.42
24.17	-	7.49	195.13	0.29	0.13	4.29	13.39	1.84	28.87

Quantification of secondary phases

S6. Calculation of carbonate yield

The quantification of carbonate phases using Rock-Eval 6 (Behar et al., 2001) involves pyrolysis and oxidation of ~40 mg of sample in an inert gas flow above 400 °C and oxidation at temperatures between 650°C–850°C. The gaseous CO_2 produced during the pyrolysis and oxidation cycles is analyzed by an infra-red analyzer (eg; S3’ peak and S5 peak respectively) in online mode and the peak areas of S3’ and S5 peaks are used to calculate the percent weight of carbonate according to the equations,

PyroMinC (wt.%)= [[S3^'* 12/44]+[S3'CO/2]*12/28]/10

OxiMinC (wt.%)= [S5*12/44]/10

The amount of total mineral carbon (MinC) in the sample is obtained by the addition of weight percent (wt.%) of mineral carbon produced from pyrolysis cycle (PyroMinC) and oxidation cycle (OxyMinC) as below,

MinC (wt.%) = PyoMinC + OxyMinC

$wt\%_{Carbonate} = MinC \; x(M_{carbonate} / M_{carbon})$, where the molar mass of carbon is 12 g/mol the molar mass of carbonates is :

- for MT1 M $((Mg_{0.92}Fe_{0.08})CO_3)$ = 86.8 g/mol
- for MT2 M $((Mg_{0.58}Fe_{0.42})CO_3)$ = 97.53 g/mol
- for MT4 M $((Mg_{0.83}Fe_{0.17})CO_3)$ = 89.7 g/mol

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	MinC	$M_{carbonate}$ g/mol	wt% Carbonate	$m_{Carbonate}$ g/kg	$n_{Carbonate}$ mol/kg	n CO_2 mol/kg	m CO2 g/kg
MT1	2.8	86.8	20.3%	225.7	2.60	2.60	114.4
MT2	6.62	97.5	53.8%	710.5	7.28	7.28	320.5
MT4	2.89	89.7	21.6%	241.6	2.69	2.69	118.5

Calculations for the amount of CO_2 trapped can be performed as follows :

$$m_{CO2\ trapped} = \frac{M_{CO2}}{M_{carbonate}} \times m_{carbonate}$$

$$m_{CO2\ trapped} = \frac{M_{CO2}}{M_{carbonate}} \times (wt\%_{carbonate} \times m_{run\ products})$$

$$m_{CO2\ trapped} = \frac{M_{CO2}}{M_{carbonate}} \times wt\%_{carbonate} \times (m_{0\ mine\ tailings} + m_{CO2\ trapped})$$

e.g. for MT2 : $m_{CO2\ trapped} = \frac{44}{97.53} \times 53.8\,\% \times (2\ g + m_{CO2\ trapped})$

$$m_{CO2\ trapped} = 0.485\ g + (0.243 \times m_{CO2\ trapped})$$

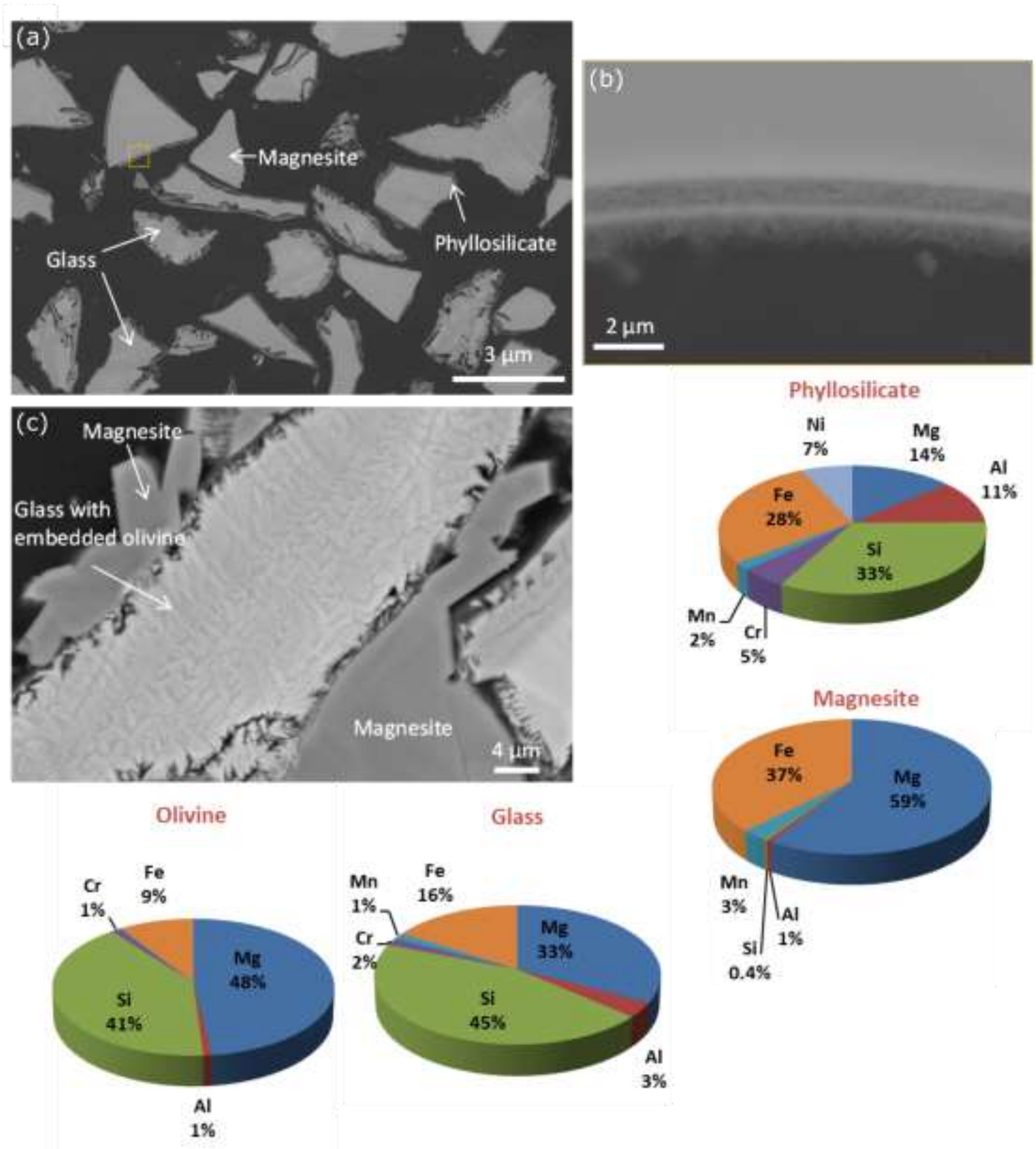
$$m_{CO2\ trapped} = 0.485\ g + (0.243 \times m_{CO2\ trapped})$$

$$m_{CO2\ trapped} = 0.641\ g\ for\ 2\ g\ of\ mine\ tailings)$$

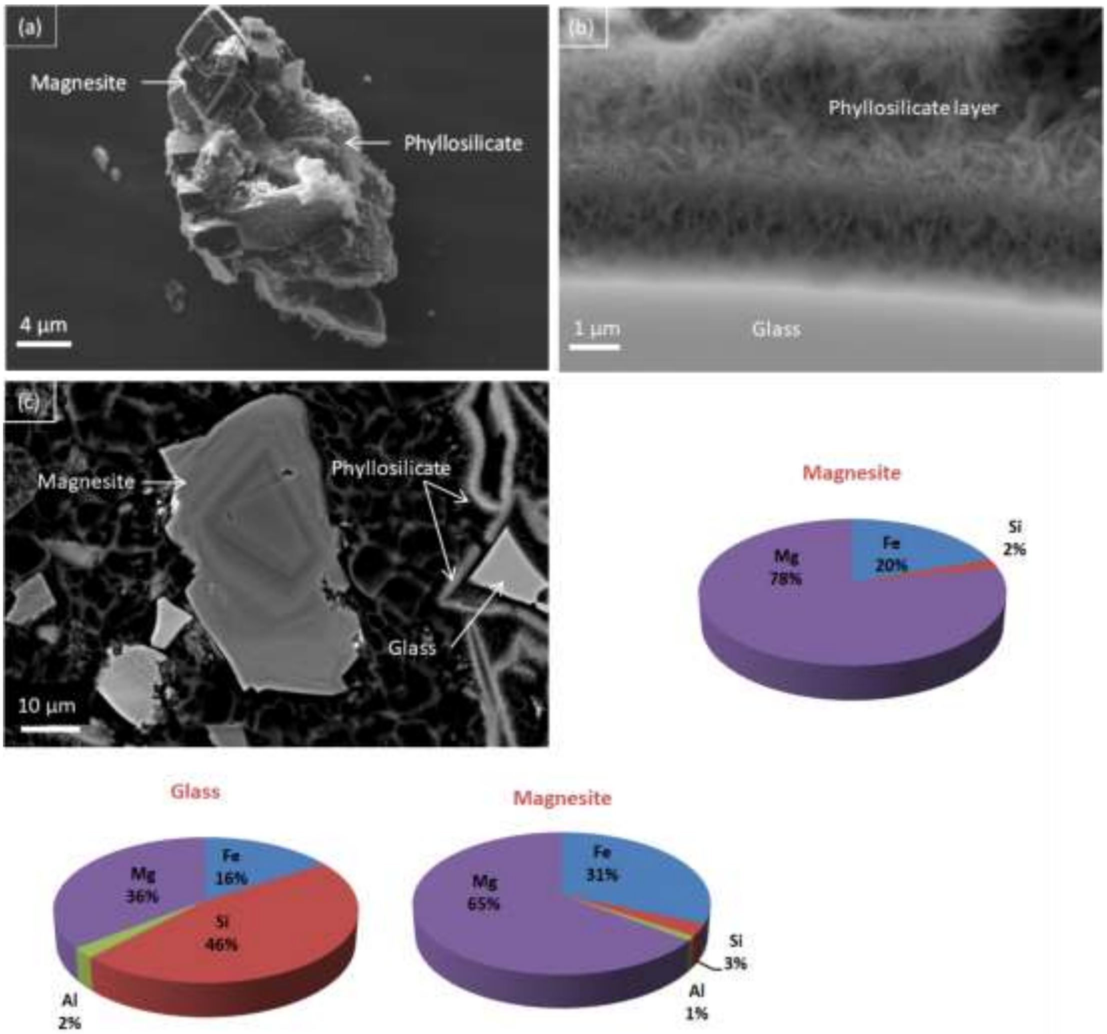
$$m_{CO2\ trapped} = 320\ g\ for\ 1\ kg\ of\ mine\ tailings$$

SEM analysis on reaction products

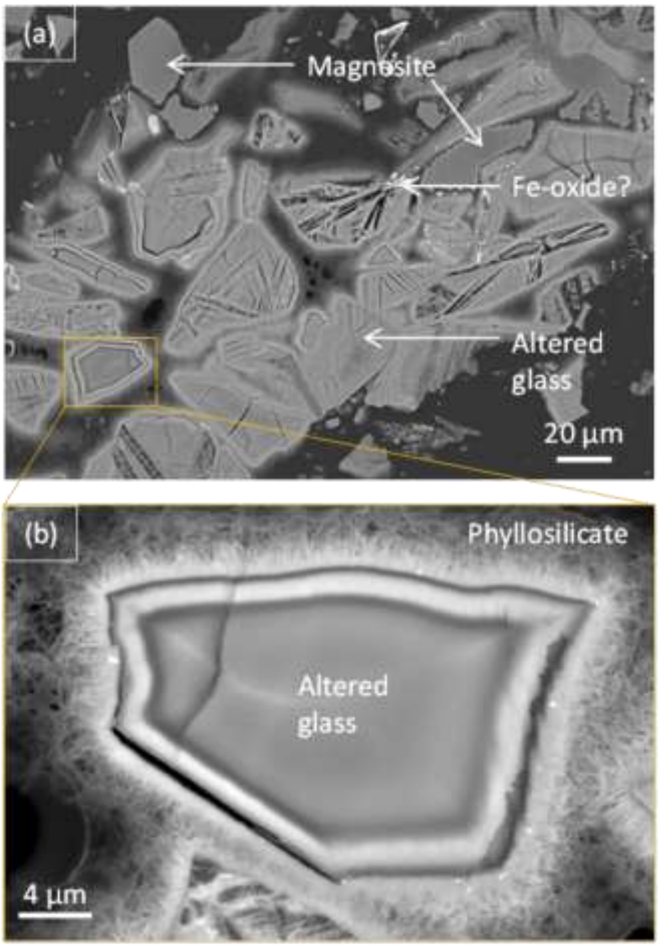
S7. SEM images of the ionically polished sections of experimental product at T = 473 K and P = 15 MPa showing large anhedral magnesite crystals grown around glass (gl) and olivine (ol). Secondary phyllosilicates (phy) layers around glass. (b) magnified image of yellow square marked on (a); (c) glass altered into magnesite; The chemical composition of phyllosilicate, magnesite, olivine and glass analyzed by SEM-EDX are shown in the pie charts.



S8. SEM images of the ionically polished sections of experimental product at T = 523 K and P = 30 MPa showing euhedral magnesite crystals and secondary phyllosilicates. (b) a magnified view of phyllosilicate (c) SEM image of a polished section of the products showing magnesite with zoning. The chemical composition obtained by SEM EDX analysis is shown in pie charts.



S9. SEM images of the ionically polished sections of experimental product at T = 573 K and P = 30 MPa, showing anhedral magnesite formed around glass, and heavily altered glass with thick layers of phyllosilicate.



S10. FIB –TEM analysis

Ultra-thin, electron transparent (<200 nm) sections of each solid reaction product was prepared by performing FIB milling at IPGP and also at Institute of Electronics, Microelectronics and Nanotechnology (IEMN), Lille using a gallium (Ga) beam. These sections which are thinned down to electron transparency (<200 nm) were then analyzed using transmission electron microscopy (TEM). For this study, we only used the composition of magnesite obtained by the TEM-EDX analysis, and the detailed mineralogical analysis of other phases, in order to understand the mineral-water interactions, is still on going.

S11. Calculation of maximum carbonation of mine tailings

Fo88	molar mass		
(Mg1.76,Fe0.24)2SiO4	148.21	g/mol	
MgO1.76 + FeO0.24	88.16		
Mg(0.8)Fe0.2CO3	87.43	g/mol	
CO2	44	g/mol	45 wt.% Fo88
MgO1.76 + FeO0.24+2CO2	176.16		79.272
Olivine + 2CO2	236.21	g/mol	106.2954
Ratio max carbonation	**74.58%**		**74.58%**
glass			
(Mg1.50,Fe0.50)2SiO3	126.45	g/mol	
MgO1.50 + FeO0.50	82.4		
Mg(0.75)Fe0.25CO3	92.125	g/mol	55 wt.% glass
CO2	44	g/mol	93.72
(Mg1.50,Fe0.50)2SiO3+CO2	170.4		117.9475
GLASS + CO2	214.45	g/mol	**79.46%**
Ratio max carbonation	**79.46%**		
		Fo88+glass	Average
		MT composit	172.992
			224.2429
		Ratio max ca	**77.14%**

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