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1 **Simultaneous ex-situ CO₂ mineral sequestration and hydrogen production**
2 **from olivine-bearing mine tailings**

3

4 ^{a,b}* **Kanchana Kularatne**

5 *corresponding author

6 ^aIFP Energies Nouvelles, 1- 4 Avenue du Bois Préau, 92852 Rueil-Malmaison, France

7 ^bInstitut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris Diderot, UMR
8 7154 CNRS, 1 rue Jussieu, F-75005 Paris, France

9 e mail : kularatne@ipgp.fr

10 Present address: Institut de Physique du Globe de Paris, 1 rue Jussieu, F-75005 Paris, France

11

12 ^a**Olivier Sissmann**

13 ^aIFP Energies Nouvelles, 1- 4 Avenue du Bois Préau, 92852 Rueil-Malmaison, France

14 e mail : olivier.sissmann@ifpen.fr

15

16 ^a**Eric Kohler**

17 ^aIFP Energies Nouvelles, 1- 4 Avenue du Bois Préau, 92852 Rueil-Malmaison, France

18 e mail : eric.kohler@ifpen.fr

19

20 ^a**Michel Chardin**

21 ^aIFP Energies Nouvelles, 1- 4 Avenue du Bois Préau, 92852 Rueil-Malmaison, France

22 e mail : michel.chardin@ifp.fr

23

24 ^a**Sonia Noirez**

25 ^aIFP Energies Nouvelles, 1- 4 Avenue du Bois Préau, 92852 Rueil-Malmaison, France

26 e mail : sonia.noirez@ifp.fr

27

28 ^b**Isabelle Martinez**

29 ^bInstitut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris Diderot, UMR
30 7154 CNRS, 1 rue Jussieu, F-75005 Paris, France

31 e mail : martinez@ipgp.fr

32

33 **Abstract**

34 Hydrothermal alteration batch experiments were conducted on olivine bearing mine tailings in
35 order to investigate two potential valorization methods: the ex-situ CO₂ sequestration and
36 hydrogen production. The originality of this work lies in the simultaneous investigation of these
37 two processes. We reacted powdered mine tailings with CO₂-saturated water at three different
38 sets of P/T conditions, 473K/ 15 MPa, 523 K/30 MPa and 573K/30 MPa. After 25 days of
39 reaction, CO₂ was sequestered in the form of Fe-bearing magnesite, (Mg,Fe)CO₃ in all the
40 experiments. Maximum carbonation yield was achieved at 523 K and 30 MPa, which was 53.8
41 wt.% of product, equivalent to the trapping of 320.5 g of CO₂ per kg of mine tailings. Hydrogen
42 gas was produced via the oxidation of Fe²⁺ in olivine. The highest quantity of hydrogen (H₂)
43 was produced at 573 K/ 30 MPa which was 0.57 g of H₂ per kg of mine tailings. It suggests that
44 the temperatures between 523 K and 540 K at pCO₂=30 MPa are favorable for simultaneous ex-
45 situ CO₂ mineral sequestration and hydrogen production from New Caledonian mine tailings.

46 The combined method of ex-situ CO₂ storage and hydrogen production proposed by
47 this study offsets 90% of New Caledonia's annual CO₂ emissions while compensating ~10 % of
48 New Caledonia's annual energy demand. More globally, it has implications for cost effective
49 disposal of industrial CO₂ emissions and production of hydrogen gas (clean energy) at a large
50 scale; those two processes could be combined using the residual heat provided by a third one
51 such as the high temperature smelting of ore.

52 Key words: New Caledonia, Nickel, Carbonation, Hydrogen, Hydrothermal, Olivine, Glass

53 1. Introduction

54 Since the industrial revolution, the atmospheric carbon dioxide (CO₂) level has been
55 substantially increased up to its present day value of ~407 ppm (NOAA, 2016), eventually
56 causing enormous climatic changes such as global warming, ocean acidification, and glacial
57 melting (Manabe and Stouffer, 1993, Kondo et al., 2018; Zhang et al., 2017; Caecer et al., 2018;
58 Marzeion et al., 2018). Up to 65% of the global CO₂ emissions were attributed to fossil fuel
59 combustion (Edenhofer et al., 2014), directing the CO₂ mitigation measures essentially towards
60 CO₂ sequestration mechanisms and introduction of alternate energy sources to fossil fuels.

61 Scientists have considered the CO₂ sequestration in minerals as the so-called permanent
62 method to capture and store industrial emissions of CO₂. This method was first suggested by
63 Seifritz (1990), based on the natural phenomena of silicate weathering into carbonates (Abu-
64 Jaber and Kimberley, 1992; Ece et al., 2005; Lugli et al., 2000; Oskierski et al., 2013; Palinkaš
65 et al., 2012; Zedef et al., 2000), during which CO₂ reacts with silicates precipitating
66 thermodynamically stable solid carbonates as given by the generalized equation below:



68 where (M²⁺) represents a divalent cation such as, Fe²⁺, Mg²⁺ and Ca²⁺ in a silicate
69 mineral, and MCO₃ thus represents the carbonate incorporating the element M. Once CO₂ is
70 converted into a carbonate following reaction (1), it will not be released into the atmosphere
71 over geological time scales.

72 For the last three decades various aspects of CO₂ mineral sequestration have been
73 experimentally investigated, on several mafic minerals such as olivine, serpentine, and
74 pyroxenes (Johnson et al., 2014; Béarat et al., 2006; King et al., 2010; Sissmann et al., 2013;
75 Daval et al., 2009a; Wolff-Boenisch et al., 2006., Park et al., 2003). Among the minerals which
76 consist of divalent Ca, Mg or Fe in their structure, olivine ((Mg,Fe)₂SiO₄) is considered the most

101 hydrogen are added to the deep sea floor by this reaction which takes place at the mid oceanic
102 ridge hydrothermal systems. A number of studies reported the temperature, thermodynamic, and
103 compositional controls on serpentinization (Janecky and Seyfried, 1986; Klein et al., 2013,
104 2009; Klein and Garrido, 2010; McCollom et al., 2016; McCollom and Bach, 2009a; Seyfried et
105 al., 2007). Two important information from these studies indicate that high temperatures (~573
106 K) favor large quantities of hydrogen due to (i) an increase of overall reaction rate of
107 serpentinization, and (ii) an increased partitioning of Fe into brucite ($\text{Mg}(\text{OH})_2$), rather than into
108 magnetite (Fe_3O_4). In addition to the hydrothermal alteration of olivine, pure iron or iron-rich
109 materials have also been experimentally studied for hydrogen production (Crouzet et al., 2017;
110 Malvoisin et al., 2013).

111 Olivine, which contains both Mg and Fe, could therefore be favorable for simultaneous
112 CO_2 mineral sequestration and hydrogen production, when reacting within a specific range of
113 pressure, temperature and pH conditions, under which carbonation and serpentinization
114 reactions will not inhibit one another. Therefore, this method is a clear improvement on current
115 CO_2 mitigation methods, as it proposes reduction of CO_2 emissions by mineral storage, and also
116 hydrogen production which is a green energy source. Compared to Fe-Mg-bearing pure minerals
117 or rocks, mine tailings serve as an alternative source of mineral alkalinity that are readily and
118 cheaply available (Bobicki et al., 2012), and can be valorized by the above method (Bobicki et
119 al., 2012; Harrison et al., 2016, 2013; Power et al., 2013; Wilson et al., 2014; Malvoisin et al,
120 2013). However, these previous studies on mine tailings have only focused on either CO_2
121 storage or H_2 production separately. The present study aims to investigate the potential of
122 combining the strategy of CO_2 mineral storage with hydrogen production by reacting olivine-
123 bearing mine waste material obtained from nickel (Ni) extraction mines in New Caledonia. In
124 order to maintain both of these reactions, the mine tailings were reacted with CO_2 -saturated
125 water at P/T range slightly inferior to the conditions previously identified as optimum for ex-situ

126 carbonation (Gerdemann et al., 2007), and close to optimum hydrogen production in
127 hydrothermal systems (McCollom et al., 2016; McCollom and Bach, 2009a; McCollom and
128 Bach, 2008; Tutolo et al., 2018; Meyhew et al., 2018). We present the quantities of CO₂ that can
129 be stored in mine tailings, and the quantities of H₂ that can be produced by this method. Based
130 on these experimental values, we estimated the CO₂ offset and compensation of energy demand
131 of New Caledonia. Although the application of this process is centered on New Caledonian mine
132 tailings, it could be translated to other industrial sites where Mg and Fe remain major
133 components of the wastes after ore processing.

134 **2. Materials and methods**

135 **2.1 Starting materials**

136 All the experiments were performed on olivine bearing mine tailings from industrial
137 nickel (Ni) extraction sites in New Caledonia, where Ni is extracted from laterite and saprolite
138 ores (Wacaster, 2013). The hand specimens of mine tailings consisted of light- to dark-green
139 irregular shaped grains with sizes ranging from few millimeters to < 1 cm. The X-ray diffraction
140 (XRD) analysis performed on a finely powdered sample indicated the presence of olivine, traces
141 of enstatite and an amorphous phase (glass). The amount of glass was quantified by XRD
142 Rietveld analysis performed on the diffraction pattern of a mixture of powdered mine tailings
143 and alumina (20 wt.%) where alumina serves as the internal standard (Bish and Howard, 1988;
144 Bish and Post, 1993; McCusker et al., 1999). According to this analysis the sample was
145 composed of 55 wt.% of glass and 45 wt.% of crystalline olivine. The chemical composition of
146 mine tailings was obtained by electron probe micro analysis (EPMA) operated at 15 keV and 40
147 nA, on few randomly selected macroscopic grains mounted on epoxy resin. The analysis was
148 performed on multiple points on glass and olivine, which appeared texturally different under
149 SEM, and the average compositions were reported in Table 1. This is in good agreement with

150 the composition reported by Bodéan et al. (2014), who used the same material for CO₂
151 sequestration experiments. The magnesium numbers ($Mg\# = Mg/(Mg+Fe)$) of the glass and
152 crystalline olivine were 0.75 and 0.88 respectively, and were calculated on molar basis using the
153 average oxide wt.%.

154 Mine tailings were crushed in a ball mill to obtain 40 - 63 μm size fraction. This size
155 fraction was chosen in order to maintain rapid dissolution kinetics, as well as to facilitate
156 microscopic observations. Furthermore, those grain sizes are in the same range than those used
157 in the few previous studies on hydrogen generation (Malvoisin et al., 2013, 2012a, 2012b), thus
158 making the comparison easier. Even though the choice of nano-scale particles could have
159 provided a considerably faster reaction, the mineral surfaces available for microscopic studies of
160 the products would have been limited. Finally, for industrial purposes, grinding large quantities
161 of solid down to the nanometer scale would largely increase the cost of the process.

162 The selected sieve fraction was subsequently ultrasonically cleaned in ethanol for 8-
163 10 min to remove the fine particles adhered to the surface. This process was repeated until the
164 supernatant became clear. The powder was dried in oven at 343 K overnight after cleaning with
165 ultra-pure de-ionized water (electrical conductivity = 18.2 MΩ cm). Very few fine particles
166 remained adhering to the grain surfaces of the above dried powder, when observed under SEM
167 (Figure 1a). The specific surface area (SSA) of the cleaned starting powder was determined by
168 Kr adsorption analysis, according to the Brunauer–Emmett–Teller (BET) method (Brunauer et
169 al., 1938), yielding a value of 0.23 m²/g.

170 Scanning electron microscopic (SEM) analysis performed on a polished section of
171 mine tailings indicate that it consists of inclusion of free and textured glass with embedded
172 olivine crystals, resulting in a “dendritic texture” or a “quench texture” (Figure 1b). The glass
173 and dendritic texture were assumed to be the result of two steps in the ore processing. The first
174 is the “calcination” performed by pre heating the ore at >1173 K for moisture removal and first

175 phase of metal oxide reduction. The second is the “fusion reduction” by which the ore is melted
176 using an electrode operated at <1973 K, separating Ni from the residue or mine tailings. We
177 assume that these conditions reached the “dry” melting-point of peridotite (-approximate
178 composition for the ophiolite) under atmospheric pressure (Takahashi, 1986), where olivine can
179 coexist with pyroxene melt up to about 2023 K at 1 atm during the eutectic melting of peridotite,
180 which could probably explain the quench texture in mine tailings.

181 **2.2 High pressure and high temperature experiments**

182 Three batch experiments were conducted at different P/T conditions, in order to
183 investigate the most favorable conditions for simultaneous CO₂ sequestration and H₂ production.
184 All the experiments were performed in 250 ml volume Parr[®] hastelloy stirring- type batch
185 reactors (impeller speed, 100 r.p.m), with a TiO₂ inner lining. Powdered mine tailings and
186 deionized water (1:100 mass ratio) were added to the batch reactors and pressurized with CO₂
187 (99.9% purity).

188 The first experiment (MT1) was conducted at 473K/ 15 MPa, which was slightly
189 above the known optimum temperature reported for the CO₂ mineral sequestration, i.e. 453 K/15
190 MPa, using a solution of 0.64M NaHCO₃/1M NaCl. The second and third experiments were
191 conducted at P/T conditions more favorable for H₂ production by serpentinization, such as 473
192 K and 673 K and 30-50 MPa (Allen and Seyfried, 2003; Andreani et al., 2012; Berndt et al.,
193 1996; Janecky and Seyfried, 1986; Malvoisin et al., 2012a; McCollom and Bach, 2009b;
194 McCollom and Seewald, 2001). These conditions are known to accelerate the serpentinization
195 rate while producing large amounts of H₂. The second experiment (MT2) was thus conducted at
196 523 K/30 MPa, both temperature and pressure being slightly above MT1. The third experiment
197 (MT4) was performed at 573 K/30 MPa. Two more experiments were conducted as blank runs
198 (MT2b, and MT4b) to determine possible contaminations in gas phase. They were conducted
199 under similar conditions (-in terms of amount of water, pCO₂, T) to those of MT2 and MT4, but

200 without any solid phases added in the reactor. Details of these experiments are reported in Table
201 2. The run duration of all the experiments was approximately 25 days. The $p\text{CO}_2$ of the
202 experiments drops intermittently (0.1 to 0.5 MPa) during the run due to; (i) CO_2 consumption by
203 carbonation reaction, and (ii) sampling out aliquots of gas from the batch reactor. The pressure
204 was re-adjusted to the initial pressure by pumping CO_2 gas back to the batch reactor. At the end
205 of the 25-days run, the experiments were quenched rapidly to ambient conditions by cooling the
206 reactor cell in a water bath for ~20-30 min. The autoclaves were then opened right after
207 releasing the pressurized CO_2 inside the reactor, minimizing the potential formation of secondary
208 products at this stage. The solid products were recovered and oven-dried at 333 K overnight,
209 then used for further analysis, as described below.

210 At these P/T conditions, most of the CO_2 pumped into the reactor exists as $\text{CO}_{2(\text{aq})}$
211 with a smaller amount of $\text{HCO}_3^-_{(\text{aq})}$ and traces of $\text{CO}_3^{2-}_{(\text{aq})}$, which can therefore be summed up to
212 a binary mixture of $\text{CO}_2\text{-H}_2\text{O}$ that has not reached critical condition. The initial pH at P/T
213 relevant to experimental conditions was calculated by the CHESS geochemical code (van der
214 Lee and De Windt, 2002) for each reaction temperature, creating a closed system with water and
215 CO_2 ($f\text{CO}_2$ at each P/T conditions was calculated using the Thermosolver program (Barnes and
216 Koretsky, 2004). The experimental conditions and the calculated initial pH of the solutions are
217 reported in Table 2.

218 **2.3 Sampling and analytical methods**

219 **2.3.1 Gas sampling and analysis**

220 The gas phase in the head space of the batch reactor was sampled every 2-3 days
221 during the reaction, by connecting a gas-sampling tube to the batch reactor. Before sampling, a
222 vacuum of 10^{-5} bars was created along the tubings of the batch reactor and also in the sampling
223 tube. The vacuum was held for about 10-15 min. This procedure ensures the absence of any leak
224 and contaminations in the tubings. Collected gas samples were then analyzed with a Varian CP-
225 3800 gas chromatograph (GC) to identify and quantify the gaseous products of the reaction. For
226 this purpose, two standards were first analyzed: one with an atmospheric composition, and the
227 other being a mixture of H₂, He, N₂, CO₂ and alkanes up to four carbons (C₁-C₄). The samples
228 and the standards were injected to the GC at ~1200 mbar at room temperature. Before analyzing
229 a standard or a sample, a blank measurement was carried out by injecting N₂. Finally, the
230 percentages (%) of each gas in the analyzed samples were calculated using the response factors
231 (k) obtained. The uncertainty on H₂, CO₂, CH₄ and other simple alkanes abundances (C₂-C₄)
232 measured by GC were 5.4%, 1.3%, 0.6% and ~1.2% respectively.

233 **2.3.2 Solid product analysis**

234 The mineralogical composition of bulk solid products was obtained through XRD
235 analysis performed on finely powdered reaction products, using a X'Pert PRO (PANalytical) x-
236 ray diffractometer with a Cu anode (Cu K α = 1.5418 Å), operated under 45 kV and 40 mA. The
237 detection limit of XRD is ~1%. Rock-Eval 6 analysis was performed for better detection and
238 quantification of carbonate. The quantification limit of Rock-Eval 6 is ~0.02 wt.% C, which
239 corresponds to ~0.15 wt.% MgCO₃; this method is one order of magnitude more sensitive than
240 the phase quantification by XRD. More details on sample preparation, instrumentation and
241 analysis of the Rock-Eval 6 technique can be found in Behar et al. (2001) and Lafargue et al.

242 (1998). The analytical details and the calculation of carbonates are reported in supporting
243 information S6. Energy dispersive X-ray analysis in transmission electron microscope (TEM-
244 EDX) was performed on ultra-thin sections prepared by focused ion beam milling (FIB), in
245 order to obtain the composition of magnesite: more details are given in supporting information
246 S10.

247 A separate fraction of the reaction products was mounted on adhesive carbon-taped
248 sample holders, gold (Au) coated and observed under “high vacuum” conventional SEM, EVO
249 MA 10, Carl Zeiss SMT with a tungsten filament operated under 15 kV and 100 mA. A 150 pA
250 beam was applied for secondary electron (SE) imaging to observe the surface topography with a
251 high spatial resolution, while the back scattered electron detector (BSE) was used to obtain
252 images with atomic number contrast. Qualitative chemical analyses were performed by energy
253 dispersive X-ray analysis (EDX), with a probe current at 700 to 750 pA (Oxford). The silicon
254 drift detector is calibrated on cobalt (Co) for quantitative analyzes during 10 s at 10 to 15 keV
255 with a dead time of about 15 s. In addition, SEM element mapping was performed on the
256 reaction products mounted on epoxy resin, finely polished by ion beam milling.

257 **2.3.3 Fe(III) / Fe(II) analysis**

258 The amounts of Fe^{2+} and total iron in the non-reacted mine tailings, and the three
259 experimental products were analyzed at the Centre de Recherches Pétrographiques et
260 Géochimiques (CRPG), Nancy, France. The samples were boiled in HF / H_2SO_4 to release Fe^{2+}
261 which was then quantified by volumetric titration with $\text{K}_2\text{Cr}_2\text{O}_7$. Another fraction of the sample
262 was then heated with LiBO_2 at 1223 K and acid digested (4 vol.% HNO_3) to convert all species
263 of iron (e.g. Fe^0 and Fe^{2+}) contained in the sample into Fe_2O_3 (Fe^{3+}). The resulting ferric iron
264 was measured by atomic absorption spectrophotometer (AAS). The amount of Fe^{3+} in the non-
265 reacted mine tailings sample was calculated by subtracting the Fe^{2+} molar amount measured in

266 the FeO analysis from the ($\text{Fe}^{2+} + \text{Fe}^{3+}$) amount measured in the Fe_2O_3 analysis. The value being
267 close to 0 suggests there is little to no oxidized iron in the initial material. The quantities of H_2
268 measured by GC at the end of the experiments were compared to the amounts calculated from
269 the loss of Fe^{2+} (through oxidation and simultaneous H_2 production) in the products. In order to
270 estimate the amount of Fe^{3+} formed during the experiments, the amount of Fe^{2+} measured in the
271 products were subtracted from the one measured in the initial non-reacted mine tailings; the
272 quantity of H_2 produced was then extrapolated from the oxidized iron (Fe^{3+}) according to:



274 where, the stoichiometric proportion of $\text{Fe}^{2+} : \text{H}_2$ is 2:1.

275 **3. Results**

276 **3.1 Secondary products**

277 XRD pattern of non-reacted mine tailings and the reaction products of three experiments are
278 shown in Figure 2c. The non-reacted mine tailings sample primarily consisted of olivine. The
279 peaks of corundum (Figure 2c), in this diffraction pattern are due to pure corundum which was
280 added to mine tailings as the internal standard for quantification of glass. The products consisted
281 of Fe-rich magnesite as the major phase, small quantities of phyllosilicates and traces of non-
282 reacted olivine (Figure 2c). Fe-bearing magnesite was identified by the characteristic reflections
283 at $2\theta = 35.9^\circ$ and 50° (Giammar et al., 2005; Garcia et al., 2010). SEM element mapping
284 performed on a polished section of MT2 sample showed the presence of abundant magnesite
285 compared to other phases such as olivine, glass, and phyllosilicate, and therefore is well in
286 agreement with the XRD results (Figure 2a). The SEM analysis performed on a carbon-coated
287 reaction product of the same sample indicates the growth of rhombohedral magnesite containing
288 both Fe and Mg, as confirmed by the EDX spectra collected on SEM (Figure 2b). Figure 3
289 shows the SEM analysis performed on polished sections of solid products of the three

290 experiments, each mounted on epoxy resin. At 473 K /15 MPa, mine tailings have been altered,
291 precipitating anhedral magnesite, and thin layers of phyllosilicate (Figure 3a). Magnesites
292 precipitated along a grain of textured mine tailings are shown on Figure 3b. At 523 K /30 MPa,
293 the product contained thick phyllosilicate layers around mine tailings and subhedral magnesite
294 with Fe and Mg compositional zoning (Figure 3c). At 573 K /30 MPa, the products contained
295 anhedral magnesites and mine tailings heavily covered by a thick fibrous phyllosilicate layer
296 (Figure 3c). More SEM images with EDX analysis on these samples are given in supplementary
297 S7, S8 and S9. The chemical composition of magnesites analyzed by TEM-EDX yielded
298 $Mg_{0.92}Fe_{0.08}CO_3$, $Mg_{0.58}Fe_{0.42}CO_3$ and $Mg_{0.83}Fe_{0.17}CO_3$ at 473 K /15 MPa, 523 K /30 MPa and
299 573 K /30 MPa respectively, showing different concentrations of iron further discussed in
300 section 4.2. The details of TEM analysis is given in supplementary information S10.

301 Compared to the diffraction pattern of the non-reacted sample, the peak intensity of
302 olivine gradually decreases with the increasing temperature of the experiments, indicating
303 olivine dissolution has mostly increased along with temperature. The semi-quantitative phase
304 analysis on the collected diffraction patterns indicated that approximately 23.3 wt.%, 9.4 wt.%
305 and 12.2 wt.% of olivine were still remaining in the reaction products of 473 K /15 MPa, 523 K
306 /30 MPa and 573 K /30 MPa experiments respectively. The peaks for phyllosilicates are broad
307 and less intense in all experiments, and the number of phyllosilicate peaks visible on the
308 diffractogram increased with temperature, indicating more phyllosilicates formed with higher
309 temperature. A preliminary identification of these phyllosilicates was obtained by applying a
310 treatment with ethylene glycol to verify their expansion properties, which suggested that they
311 were smectite clay minerals. However, due to the inherent limitations of the equipment, the
312 amount of phyllosilicate and remaining glass could not be quantified separately.

313

314

315 **3.2 Carbonate yield**

316 The presence of carbonates and their precise quantification were further confirmed using the
317 Rock-Eval 6 technique. The only carbonate phase produced in all the experiments were Fe-
318 bearing magnesites, $(\text{Mg,Fe})\text{CO}_3$, in accordance with the results of XRD analysis. Carbonate
319 quantification by Rock-Eval 6 resulted in 20.3%, 44.9% and 21.6% at 473 K/ 15 MPa, 523 K/
320 30 MPa and 573 K/ 30 MPa respectively (the calculation is given in S6); those carbonation
321 yields are averages of duplicate experiments. These yields suggest that 1.00 kg of mine tailings
322 could capture 115g, 321g and 119 g of gaseous CO_2 by a reaction with pure water at 473 K/ 15
323 MPa, 523 K/ 30 MPa and 573 K/ 30 MPa, respectively (Table 2 and S6).

324 **3.3 Hydrogen production**

325 As the starting mine tailings material is iron-rich (average of 10.9 wt.%), its reaction
326 with water at high pressure and high temperature leads to the production of H_2 , as a result of
327 iron oxidation through water reduction (also written for the serpentinization reaction given by
328 eq.3). However, the produced hydrogen in all the experiments is approximately three orders of
329 magnitude lower than the CO_2 in the gas phase, since CO_2 was injected to reach a total pressure
330 of either 15 or 30 MPa. The variations in gas phase composition in each experiment are given
331 below.

332 **At 473 K and 15 MPa:** Figure 4a, illustrates the cumulative production of hydrogen as a
333 function of time for MT1. Hydrogen was produced gradually reaching a maximum of 20.0
334 $\mu\text{mol/g}$ of mine tailings after 25 days of reaction, which indicates that the reaction is still in
335 progress. The maximum hydrogen production of 20.0 $\mu\text{mol/g}$ is equivalent to producing around
336 0.04 g of H_2 for 1.0 kg of mine tailings. Hydrogen was produced at a rate of approximately 0.7
337 $\mu\text{mol/g/day}$, obtained by the gradient fitted though the data. Traces of methane ($<0.30 \mu\text{mol/g}$)

338 were detected in the gas phase after 9.8 days of reaction, but other light hydrocarbons (C₂-C₄)
339 were not detected (S 1).

340 **At 523 K and 30 MPa:** The cumulative hydrogen production as a function of reaction time of
341 MT2 experiment is shown in Figure 4b. Hydrogen continues to be produced at a rate of 1
342 $\mu\text{mol/g/day}$ until ~ 9 days, as the reaction proceeds. After 9 days, hydrogen production increases
343 abruptly and then continues to increase at a rate of $3.2 \mu\text{mol/g/day}$. The maximum amount of
344 gaseous hydrogen measured in this experiment was $117.6 \mu\text{mol/g}$ or 0.24 g/kg of mine tailings,
345 which is approximately 5 times more than in MT1. No hydrogen was detected in the gas phase
346 of an experimental blank (MT2b) conducted under the same without adding mine tailings
347 confirming that hydrogen was produced only by reaction between pure water and mine tailings
348 (Figure 4b). Light hydrocarbons such as CH₄, C₂H₆, C₃H₈ and C₄H₁₀ were also observed in the
349 gas phases of both the experiment and experimental blank, but in trace quantities (S2 and S4).

350 **At 573 K and 30 MPa:** Cumulative hydrogen production of MT4 experiment is shown in
351 Figure 4c. At the initial stage, hydrogen was produced at a rate of $21 \mu\text{mol/g/day}$ ($0 < t < 8.8$ days),
352 reaching a maximum of $283.5 \mu\text{mol/g}$ or 0.57 g/kg . This is the highest quantity of hydrogen
353 produced among all three experiments, and is confirmed by the H₂ production inferred from iron
354 (III) measured at the end of the experiments ($265 \mu\text{mol/g}$, see Table 2). Then, the amount of
355 hydrogen decreased drastically, reaching a plateau with an average of $41 \mu\text{mol/g}$ (Figure 4c).
356 Similarly to MT2, hydrogen was not detected in the gas phase of an experimental blank (MT4b)
357 conducted at the same P/T conditions, which confirmed there was no contamination of hydrogen
358 in the experiment (Figure 4c and S3). This decrease in cumulative hydrogen could be explained
359 by the formation of short-chained organic molecules through its interaction with CO₂, as
360 discussed by Seewald (2006). In addition, CH₄, C₂H₆, C₃H₈ and C₄H₁₀ were detected in the gas
361 phase, in which the detected methane was above the 10% uncertainty of the concentration
362 detected in the experimental blank (S5).

363 **3.4 H₂ production estimated by Fe(III)/Fe(II) analysis**

364 As previously stated, hydrogen is produced via the oxidation of Fe²⁺ in the starting
365 material according to equation 4 (section 2.3.4). Therefore, the difference between the amounts
366 of FeO measured in the starting material and the reaction products quantifies the Fe²⁺ that has
367 been oxidized at high pressure and high temperature.

368 The analysis shows that the starting mine tailings sample contained, 1.3 mmol/g of
369 FeO, whereas the reaction products of MT1, MT2 and MT4 experiments contained 1.3, 1.1 and
370 0.8 mmol/g of FeO, respectively. According to this result, the initial mine tailings and the MT1
371 experiment contained the same amount of FeO, meaning that no Fe²⁺ oxidation took place.
372 However, 20 μmol/g of hydrogen was detected in the gas chromatography analysis of this
373 experiment. This could possibly suggest an analytical error in detecting such a low level of FeO
374 quantity due to the detection limit of the method used. The H₂ production estimated from the
375 stoichiometric ratio with Fe³⁺ (given in eq. 4) are reported in Table 3 for the three experimental
376 runs. Except for MT1, the estimated values of hydrogen are in good agreement with those
377 observed in gas chromatography analysis.

378 Moreover, if all the Fe²⁺ in initial mine tailings (i.e. 1.3 mmol/g) was to completely
379 oxidize into Fe³⁺, then following the equation 4 (1 mole of H₂ produced for 2 moles of Fe²⁺
380 oxidized), it could produce 655 μmol of H₂ per one gram of mine tailings. This value can be
381 used to calculate the reaction progress with respect to Fe oxidation in the system. Although the
382 value for MT1, as mentioned earlier, is too low and thus unreliable to be properly exploited, the
383 estimation shows that MT2 and MT4 reach 17.6 % and 40.5% completion of reaction
384 respectively (see Table 3).

385 **4. Discussion**

386 **4.1 Preferential dissolution of olivine within mine tailings at 473-573 K and 15-30 MPa**

387 The suitability of geological material as carbon sequestration and hydrogen production
388 feedstocks depends primarily on their reactivity and chemical composition (Power et al.,
389 2013). Mafic and ultramafic rocks are rich in Ca^{2+} , Mg^{2+} and Fe^{2+} , and therefore, are the ideal
390 sources for this purpose. New Caledonian mine tailings contained abundant Mg^{2+} and Fe^{2+} ,
391 and thus their chemical composition and reactivity favored CO_2 sequestration and hydrogen
392 production. Mineral dissolution, is essentially the first step that makes Mg^{2+} and Fe^{2+}
393 available for both carbonation and hydrogen production reactions, and is a function of crystal
394 chemistry, particle size of reacting mineral, pH, and temperature. As shown in Figure 2,
395 olivine dissolved gradually with increasing temperature of our experiments, indicating that for
396 our grain sizes and pH, increasing temperatures were favoring the dissolution of olivine.
397 Inevitably, XRD pattern does not indicate the dissolution of glass due to its lack of
398 crystallinity. In acidic to neutral pH, the dissolution kinetics of olivine have been reported to
399 be faster than that of basaltic glass, which is an approximation that can be made for mine
400 tailings (Gudbrandsson et al., 2011; Wolff-Boenisch et al., 2006; Wolff-Boenisch et al., 2011).
401 These two previous studies suggest that, under acidic conditions such as those of our study,
402 the constituent minerals of crystalline basalt dissolve faster than basaltic glass by more than
403 one order of magnitude (olivine, a nesosilicate with a Q_0 structure, has all silicate tetrahedrons
404 disconnected from each other, as opposed to glass, and thus faster dissolution kinetics). This
405 indicates that olivine is the major contributor to the Mg^{2+} and Fe^{2+} cations in the solution.

406 **4.2 Reaction path and formation of secondary Mg-silicates**

407 The XRD patterns of the products indicated that the reaction of mine tailings with
408 CO_2 -saturated water, resulted in Fe-rich magnesite, and small quantity of phyllosilicates.

409 Hydrogen is the gaseous product of this reaction. Hematite (Fe_2O_3) was observed only in MT4
410 (573 K/30 MPa) experiment. Although, we anticipated the production of hydrogen through
411 serpentinization reaction, our result showed that the products of the reaction after 25 days
412 consisted of smectites. However, formation of proto-serpentine-like phase using New
413 Caledonian mine tailings was reported by Bodénan et al. (2014), in an experimental work
414 where 1-day reactions took place either in water or in a 0.43 M NaCl/0.27 M NaHCO_3
415 solution at 453 K at a $p\text{CO}_2$ of 1-9 MPa.

416 The difference between the reaction products of those two sets of experiments
417 cannot be explained by different pH conditions, as Bodénan et al.(2014) run experiments both
418 in bicarbonate solution (which has the buffer ability to remain neutral under $p\text{CO}_2$ pressure),
419 and in deionized water (which becomes acidic). The temperature, though lower in Bodénan et
420 al.'s study (453K), remains close to our study's conditions (473-573K), and grain size (which
421 influences specific surface area) should not have a critical influence on thermodynamic
422 equilibrium. With respect to these parameters, the two studies are comparable, while their
423 reaction products differ. One possible explanation could very well lie in the duration of the
424 experiments. A study investigating the genesis of ultramafic hosted magnesite vein deposits
425 by Abu-Jaber and Kimberly (1992) has reported, within natural samples, on the reaction of
426 serpentine, magnetite and bicarbonate into (Fe-)nontronite (smectite) and magnesite.
427 Furthermore, a recent experimental study describes various pathways for the conversion of
428 serpentine to smectite under hydrothermal conditions, during which Al^{3+} substitutes to Si^{4+} .
429 They suggest that solid-state transformation is the main mechanism involved. Since this is a
430 process is kinetically limited, the difference in the experiments duration (1 day for Bodénan et
431 al. vs 25 days for this study) could explain the different reaction product. Serpentine would
432 therefore only be an intermediate phase.

433

434 **4.3 Fe-rich magnesite precipitation and hydrogen production**

435 Fe-rich magnesite was the only carbonate precipitated in our experiments as
436 confirmed by XRD and Rock-Eval 6 analysis. Theoretically, mine tailings could precipitate a
437 maximum of 77 wt.% of magnesite, assuming 100% dissolution of mine tailings (S11). The
438 quantities of Fe-rich magnesite precipitated at 473 K/15 MPa, 523 K/30 MPa and 573 K/30
439 MPa were 20.3, 44.9 and 21.6 wt.%, respectively. If the reaction completion (Rx) with respect
440 to carbonate precipitation is given by the ratio between the observed carbonate wt.% versus
441 the calculated maximum carbonate wt.%, then 26.4%, 58.3% and 28.1% of reaction
442 completion were achieved respectively during the experiments. Interestingly, the iron content
443 in magnesite followed the same trend as reaction completion, with 0.08, 0.58 and 0.17 moles
444 of iron in one mole of magnesite at 473 K/15 MPa, 523 K/30 MPa and 573 K/30 MPa
445 respectively. This would indicate that the lower temperature and low $p\text{CO}_2$ in MT1 (473 K/15
446 MPa) slowed down kinetics of the dissolution and precipitation reactions resulting in low
447 quantities of magnesite with small quantity of iron, compared to the other two experiments.
448 The MT2 and MT4 experiments, which were conducted at same $p\text{CO}_2$ (30 MPa), revealed that
449 almost all the olivine dissolved at increasing temperature up to 573 K. But, the precipitated
450 magnesite at 523 K was twice higher than at 573 K. As Mg is the major element in magnesite,
451 this result clearly indicates the competition of Mg incorporation into magnesite vs. secondary
452 Mg-silicates in the 523-573 K temperature range. In addition, the quantity of iron
453 incorporated in magnesite at 523 K is twice as high than at 573 K, indicating that
454 temperatures between 523 -573K favored the incorporation of iron into other phases than
455 magnesite. As shown by Andreani et al. (2012), the fast precipitation of Al-Fe-rich serpentines
456 indeed competes with magnetite nucleation and may indeed inhibit it altogether. Nevertheless,
457 magnetite formation is enhanced with increasing temperature, as shown by Malvoisin et al.,
458 2012); those studies thus support the present observations and findings on Fe(III)

459 incorporation into secondary phases. Total iron (II+III) incorporation into secondary phases
460 and its correlation with hydrogen production is also worth mentioning because it demonstrates
461 the competition between two other reactions in the system: the iron incorporation into
462 magnesite versus secondary Mg-silicates (\pm iron oxides). As the temperature increased from
463 523 K to 573 K, hydrogen production was approximately doubled, producing more Fe^{3+} . At
464 523 K, the most likely secondary phase to host Fe^{3+} was secondary phyllosilicate, whereas at
465 573 K, it could possibly be incorporated into phyllosilicate and into iron (III) oxides as well.
466 Although, ferric-hydrate complexes could host Fe^{3+} ions, we assumed their quantities to be
467 negligible. Magnesite structure accommodates only Fe^{2+} . Therefore, the results clearly
468 indicate that temperatures between 523 -573K favor iron oxidation, whereas temperatures
469 between 473 K and 523 K favor the iron incorporation into magnesite. The competition
470 between Mg and Fe incorporation among the secondary phases seems to control the quantities
471 of magnesite precipitation and hydrogen production. Moreover, Figure 5, which shows the
472 magnesite production (in wt.%) versus hydrogen production clearly demonstrates that
473 temperatures between 523 K and 540 K at $p\text{CO}_2=30$ MPa (shown by shaded area) would be
474 the most favorable conditions for reacting mine tailings in order to maintain both carbonation
475 and hydrogen production in significant quantities. Although the P/T conditions of maximum
476 carbonation in our experiments differ slightly from those of Gerdermann et al. (2007), it can
477 be argued that this discrepancy arises from the different solutions used in two studies; a CO_2 -
478 saturated water here compared with a 0.64M NaHCO_3 , 1M NaCl solution in Gerdermann et
479 al. (2007). Furthermore, Andreani et al. (2012) and Sissmann et al. (2013) mention the effect
480 of aluminum on dissolution kinetics of olivine dissolution kinetics. Its presence in the
481 associated glass phase of the mine tailings could also slightly change not only those
482 dissolution kinetics but also the precipitation kinetics of carbonates.

483 The analysis of FeO in the starting material and the products were used to evaluate
484 the amount of iron oxidation, and to further confirm the hydrogen amounts measured by gas
485 chromatography. As mentioned in section 3.4, the Fe(III) / Fe(II) analysis of non-reacted mine
486 tailings confirmed that the starting material does not contain any Fe³⁺ that could have resulted
487 from ore processing. Assuming the mine tailings have been well homogenized after crushing
488 and sieving, the Fe²⁺ measured in the experimental products was expected to be lower than in
489 the initial sample, due to the oxidation of Fe²⁺ during the experiment. However, the amount of
490 Fe²⁺ measured for MT1 is slightly above the value measured for the initial non-reacted
491 sample. Such an inconsistency could be explained by potential inhomogeneities caused by a
492 sampling bias of the starting material or the products, or due to detection limit for low Fe
493 concentrations in this sample. Nevertheless, the estimated hydrogen production from MT2
494 and MT4 experiments are in good agreement with the measured hydrogen quantities using gas
495 chromatography (Table 3).

496 The variation of hydrogen production as a function of reaction time (Figure 4)
497 indicates that the hydrogen production at 473 K/15 MPa and 523 K/ 30 MPa continued to
498 increase steadily until the end of the experiment, whereas at 573 K/30 MPa, it suddenly
499 decreased after 9 days of reaction, reaching a plateau. This result suggests that at the lower
500 temperatures, the production on of H₂ is not buffered by new secondary phases (no
501 phyllosilicates passivating the surface of mine tailings). However, at 573K, it appears that
502 hydrogen production is being buffered. A possible explanation would be the limitation of Fe²⁺
503 supply, and thus of further water reduction and H₂ production. Nevertheless, the sharp
504 decrease in H₂ concentration followed by a plateau could indicate that a steady state has been
505 reached, and that H₂ is being consumed to form light organic compounds dissolved within the
506 system (not quantified in this study) through a reaction with CO₂.

507

508 **4.4 Carbonation and hydrogen production from mine tailings vs. other slags**

509 First our results on CO₂ sequestration were compared with two experimental
510 studies by Bobicki et al. (2015) and Garcia et al. (2014), who conducted experiments at
511 T~423 K and PCO₂ ~15 MPa. Bobicki et al. (2015) used chrysotile from two nickel (Ni)
512 mines (Okanogan nickel deposit in Washington State, USA (OK ore) and Thompson Nickel
513 Belt in Manitoba, Canada, (Pipe ore), respectively) (table 4). The ores contained 6.0 and 7.8
514 wt.% of MgO, with approximately <7 wt.% of CaO+FeO. In contrast, Garcia et al. (2010)
515 used pure olivine (Fo91), with 55.5 wt.% of MgO (theoretical), which is also close to the
516 average MgO content of this study (53.6 wt.%), but containing nearly half of the iron
517 compared to mine tailings in this study (12.95 wt.%). Our results on carbonation yields lie
518 within the same order of magnitude compared to the two studies considered here. However,
519 despite the large granulometry of the starting materials, Bobicki et al. (2015) was able to store
520 CO₂ at a higher rate (~200 g/kg CO₂ within one hour) than the other two studies. They reacted
521 olivine (formed from the reversion of heat-treated chrysotile) at the conditions previously
522 suggested by Gerdemann et al. (2007), making solution salinity and bicarbonate concentration
523 the main differences with the other two studies. This suggests that the rate of CO₂ storage in
524 our experiments could have been enhanced if such high concentrations had been used.
525 However, even though the rate was slower, MT2 experiment stored more CO₂ compared to
526 Bobicki et al. (2015) and Garcia et al. (2010).

527 It is highly probable that the higher temperature range presumably limits
528 carbonation, while the lower range limits H₂ production. The higher temperatures increase
529 dissolution kinetics, leading to a larger amount of silica in solution. As that silica precipitates,
530 they form secondary phyllosilicates that scavenge the divalent cations (equation 3). In
531 contrast, the lower temperatures create lower silica supersaturation, and the cations enter
532 carbonate phases leaving less iron available for oxidation and hydrogen production (equation

533 2). Nevertheless, this study proves that intermediate conditions can be set to make both
534 processes work simultaneously.

535 The amounts of hydrogen produced in our experiments were compared with two
536 similar studies (Crouzet et al., 2017; Malvoisin et al., 2013), who attempted to produce
537 hydrogen by using pure wüstite (FeO) and Fe-rich steel slag (Table 5). For the sake of
538 comparison, hydrogen produced at 473 K or 573 K, and 30 MPa after ca. 69 or 160 hours of
539 each study were used. The study by Malvoisin et al. (2013) used a carbonated basic oxygen
540 furnace (CARBOF) containing 2.7 wt.% Fe(0), 20.58 wt.% FeO and 3.16 wt.% Fe₂O₃. The
541 grain size of original steel slag used for carbonation was 1 -50 µm. The second study (Crouzet
542 et al., 2017) is a follow-up study of Malvoisin et al. (2013) that investigates the hydrogen
543 production under acidic pH conditions using 50-100 µm size pure wüstite (FeO). Because the
544 chemical composition of steel slag, wüstite and New Caledonian mine tailings largely differ
545 from each other, we calculated the hydrogen production per mass unit of FeO of each
546 material. In our study, the hydrogen measured by gas chromatography, and average FeO in
547 mine tailings (12.95 wt.%) were used for this calculation.

548 As shown in Table 5, H₂ production seems to be correlated with pH: the lower it is, the
549 higher the amount of H₂ generated. This can be explained by the fact that low pH promotes
550 mineral dissolution and thus Fe²⁺ release. Thus, at a similar temperature (573K), this study
551 (pH 3.9) generates more H₂ than Crouzet (pH 6.0), which generates more than Malvoisin (pH
552 6.9). However, the pH effect is not the only way to increase H₂ production. As shown by
553 Crouzet et al. (2017), the addition of organic ligands (such as acetic acid) can increase H₂
554 generation even further by promoting mineral dissolution.

555

556 **4.5 Implications for CO₂ sequestration and hydrogen production in New Caledonian**
557 **mining sites and other Ni mining sites**

558 New Caledonia is the 11th largest Ni producer in the world, preceded by the United
559 states, Australia, Brazil, Canada, China, Columbia, Cuba, Guatemala, Indonesia and
560 Madagascar (U.S. Geological Survey, 2017). When scaled to land area, however, its
561 production of Nickel is in the top 3, implying a high environmental fingerprint. In 2013, New
562 Caledonia produced 127,027 metric tons (t) of nickel from 7.8 million metric tons (Mt) of
563 saprolite ore and 36,839 t of nickel from 4.2 Mt of laterite ore, resulting approximately in 12
564 million metric tons (Mt) of mine tailings per year (Wacaster 2013). The management of mine
565 tailings such as collection, storage and re-usage are costly to process. Currently these mine
566 tailings are used for geo-technical aspects such as building roads, dams, and land filling.
567 Compared to the traditional valorization methods, those proposed by this study are novel and
568 might be used to contribute to today's always-increasing energy demands, by producing an
569 energy source through waste recycling. In addition, implementing a simultaneous ex-situ CO₂
570 storage and hydrogen production plant in the vicinity of mining sites provides a safe and
571 permanent disposal of CO₂ emitted by the nickel industry. Although the chemical looping
572 processes have been documented for carbon capture and storage (Bui et al., 2018; Cormos,
573 2017), the idea of energy looping does not appear prominently in literature. It is nevertheless
574 our belief that inspiration could be drawn from chemical looping: the energy needed for
575 heating the material could be obtained passively by locating this plant near high temperature
576 furnaces used for ore-processing.

577 The annual CO₂ emission of New Caledonia is about 4.3 Mt/y (Boden et al.,
578 2017). Our experiments having shown that at 523 K and 30 MPa, mine tailings can trap at
579 least 320 g of CO₂ per kg of mine tailings (supporting information S6), it follows that the

580 annual mine tailings production could potentially trap 3.8 Mt/y of CO₂, which represents
581 about 90% of New Caledonia's annual emissions.

582 The annual electrical consumption of New Caledonia is approximately 2400 GWh;
583 (New Caledonia Department of Energy, 2013). The maximum hydrogen production in our
584 experiments was 0.57 g hydrogen per kg of mine tailings at 573 K and 30 MPa. According to
585 this value, the annual mine tailings produced in New Caledonia is able to produce 6840 tons
586 of hydrogen per year, which is equivalent of generating 229 GWh/y (with H₂ combustion
587 generating around 120.5 MJ/kg or 33.5 kWh/kg). It represents around 10 % of New
588 Caledonia's annual electrical consumption. Furthermore, assuming an average family
589 consumes 3400 kWh/y (New Caledonia Department of Energy, 2013), the energy produced
590 would be sufficient to sustain around 67350 families.

591 One limiting factor regarding this method is the separation of small quantities of
592 hydrogen from CO₂ in the reactor. Separating CO₂ and H₂ from industrially important gas
593 mixtures (synthesis gas or natural gas) are widely performed using membrane methods
594 (Korelskiy et al., 2015). These membranes could be either made from polymers (Ghadimi et
595 al., 2014; Rabiee et al., 2014), or ceramic (Korelskiy et al., 2015), and they provide cost
596 effective means of separating gases in large scale. In our opinion, a membrane method would
597 be suitable to separate hydrogen from CO₂ in this process.

598 We believe that the simultaneous application of ex-situ CO₂ sequestration and
599 hydrogen production using New Caledonian mine tailings could be easily applied to various
600 mining industries of mafic rocks, which presumably produce mine wastes of similar
601 compositional and mineralogical characteristics. By using the residual heat provided by a
602 third process such as the high temperature smelting of ore, those two processes could be
603 translated into a high-value, cost-effective industrial way of storing wastes and generating
604 clean energy.

605 **5. Conclusions**

606 Batch experiments conducted between 473 K - 573 K under high pCO₂ of 15-
607 30 MPa have demonstrated the viability of using New Caledonian mine tailings in ex-situ
608 carbonation process, while producing H₂ as a byproduct. The results suggest that mine tailings
609 were altered into Fe-rich magnesite and phyllosilicates when reacted with CO₂-saturated
610 water at the above mentioned conditions. We have outlined that the competition between Mg
611 and Fe incorporation among the secondary phases seems to control the quantities of magnesite
612 precipitation and hydrogen production. Taken together, these results suggest that the
613 temperatures between 523 K and 540 K at pCO₂=30 MPa would be the most favorable
614 conditions for reacting mine tailings in order to maintain both carbonation and hydrogen
615 production in significant quantities.

616 This work suggest a method to treat New Caledonia's annual CO₂ emissions and
617 energy demands cost-efficiently by recycling the heat used in metal extraction (>1273 K),
618 providing a novel valorization method for New Caledonian mine tailings. This approach can
619 be globally applied to nickel (Ni) mine tailings as well as other industrial waste materials
620 containing Ca, Mg, and Fe; however we believe that the optimum P/T conditions might vary
621 depending on the mineral composition and textural features of individual material.

622

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873 **Supporting information for the manuscript entitled;**

874 **Simultaneous ex-situ CO₂ mineral sequestration and H₂ production from New**

875 **Caledonian mine tailings**

876 Kanchana Kularatne^{a,b (*)}, Olivier Sissmann^a, Eric Kohler^a, Michel Chardin^a, Sonia Noirez^a,

877 Isabelle Martinez^b

878 ^aIFP Energies Nouvelles, 1- 4 Avenue du Bois Préau, 92852 Reuil-Malmaison, France

879 ^bInstitut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris Diderot, UMR

880 7154 CNRS, 1 rue Jussieu, F-75005 Paris, France

881 **Gas phase data**

882 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	-

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884 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)	($\mu\text{mols/g}$)	($\mu\text{mols/g}$)	(mmols/g)	(mmols/g)	(mmols/g)	($\mu\text{mols/g}$)	($\mu\text{mols/g}$)	($\mu\text{mols/g}$)	($\mu\text{mols/g}$)
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	-	-	-	-	-	-

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888 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)	($\mu\text{mols/g}$)	($\mu\text{mols/g}$)	(mmols/g)	(mmols/g)	(mmols/g)	($\mu\text{mols/g}$)	($\mu\text{mols/g}$)	($\mu\text{mols/g}$)	($\mu\text{mols/g}$)
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

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893 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
894 conditions in comparison with MT2, without introducing mine tailings in the reactor (due to technical difficulties, CO₂ was not readjusted after
895 the first sampling).

MT2b									
Duration	H₂	CH₄	CO₂	N₂	O₂	C₂H₆	C₃H₈	iC₄H₁₀	nC₄H₁₁
(days)	(μmol/g)	(μmol/g)	(mmol/g)	(mmol/g)	(mmol/g)	(μmol/g)	(μmol/g)	(μmol/g)	(μmol/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

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902 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
 903 monitor H₂ and CH₄ concentrations. It was conducted at similar PT conditions in comparison with MT4, without introducing mine tailings in the
 904 reactor (due to technical difficulties, CO₂ was not readjusted after the first sampling).

MT4b									
Duration	H₂	CH₄	CO₂	N₂	O₂	C₂H₆	C₃H₈	iC₄H₁₀	nC₄H₁₁
(days)	(μmol/g)	(μmol/g)	(mmol/g)	(mmol/g)	(mmol/g)	(μmol/g)	(μmol/g)	(μmol/g)	(μmol/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

905

906 **Quantification of secondary phases**

907 **S6. Calculation of carbonate yield**

908 The quantification of carbonate phases using Rock-Eval 6 (Behar et al., 2001) involves
909 pyrolysis and oxidation of ~40 mg of sample in an inert gas flow above 400 °C and oxidation
910 at temperatures between 650°C–850°C. The gaseous CO₂ produced during the pyrolysis and
911 oxidation cycles is analyzed by an infra-red analyzer (eg; S3' peak and S5 peak respectively)
912 in online mode and the peak areas of S3' and S5 peaks are used to calculate the percent
913 weight of carbonate according to the equations,

914

915
$$\text{PyroMinC (wt.\%)} = \frac{[S3' \cdot 12/44] + [S3'CO/2] \cdot 12/28}{10}$$

916
$$\text{OxiMinC (wt.\%)} = \frac{[S5 \cdot 12/44]}{10}$$

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

920
$$\text{MinC (wt.\%)} = \text{PyoMinC} + \text{OxyMinC}$$

921
$$\text{wt\% Carbonate} = \text{MinC} \times \left(\frac{M_{\text{carbonate}}}{M_{\text{carbon}}} \right)$$
, where the molar mass of carbon is 12 g/mol the
922 molar mass of carbonates is :

923 - for MT1
$$M((\text{Mg}_{0.92}\text{Fe}_{0.08})\text{CO}_3) = 86.8 \text{ g/mol}$$

924 - for MT2
$$M((\text{Mg}_{0.58}\text{Fe}_{0.42})\text{CO}_3) = 97.53 \text{ g/mol}$$

925 - for MT4
$$M((\text{Mg}_{0.83}\text{Fe}_{0.17})\text{CO}_3) = 89.7 \text{ g/mol}$$

926

927 -

	MinC	M_{carbonate} g/mol	wt% Carbonate	m Carbonate g/kg	n Carbonate mol/kg	n CO₂ 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

928 Calculations for the amount of CO₂ trapped can be performed as follows :

$$m_{CO_2 \text{ trapped}} = \frac{M_{CO_2}}{M_{carbonate}} \times m_{carbonate}$$

$$m_{CO_2 \text{ trapped}} = \frac{M_{CO_2}}{M_{carbonate}} \times (wt\%_{carbonate} \times m_{run \ products})$$

$$m_{CO_2 \text{ trapped}} = \frac{M_{CO_2}}{M_{carbonate}} \times wt\%_{carbonate} \times (m_{0 \ mine \ tailings} + m_{CO_2 \ trapped})$$

929 e.g. for MT2 : $m_{CO_2 \text{ trapped}} = \frac{44}{97.53} \times 53.8 \% \times (2 \ g + m_{CO_2 \ trapped})$

$$m_{CO_2 \text{ trapped}} = 0.485 \ g + (0.243 \times m_{CO_2 \ trapped})$$

$$m_{CO_2 \text{ trapped}} = 0.485 \ g + (0.243 \times m_{CO_2 \ trapped})$$

$$m_{CO_2 \text{ trapped}} = 0.641 \ g \ \text{for } 2 \ g \ \text{of mine tailings}$$

$$m_{CO_2 \text{ trapped}} = 320 \ g \ \text{for } 1 \ kg \ \text{of mine tailings}$$

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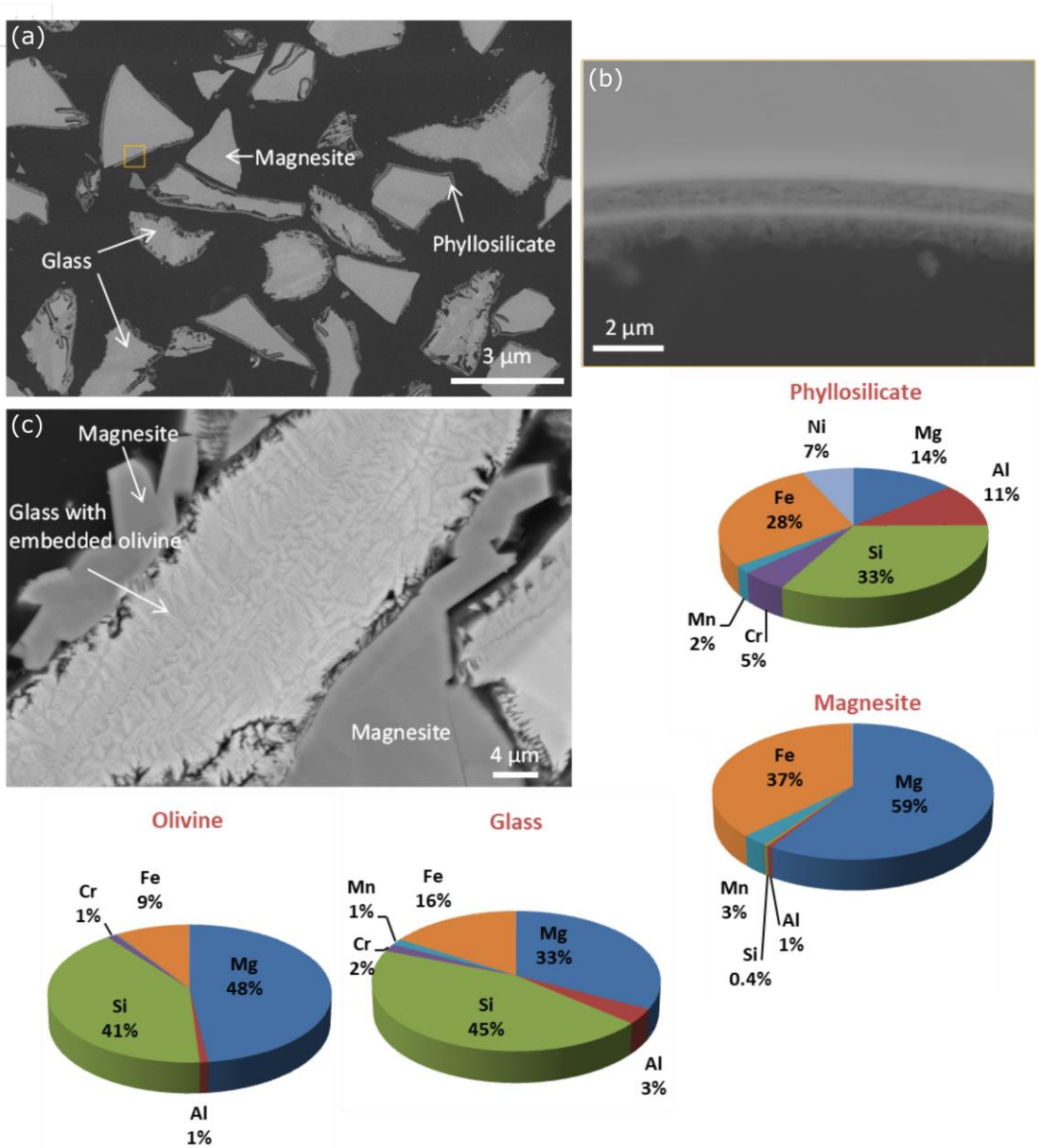
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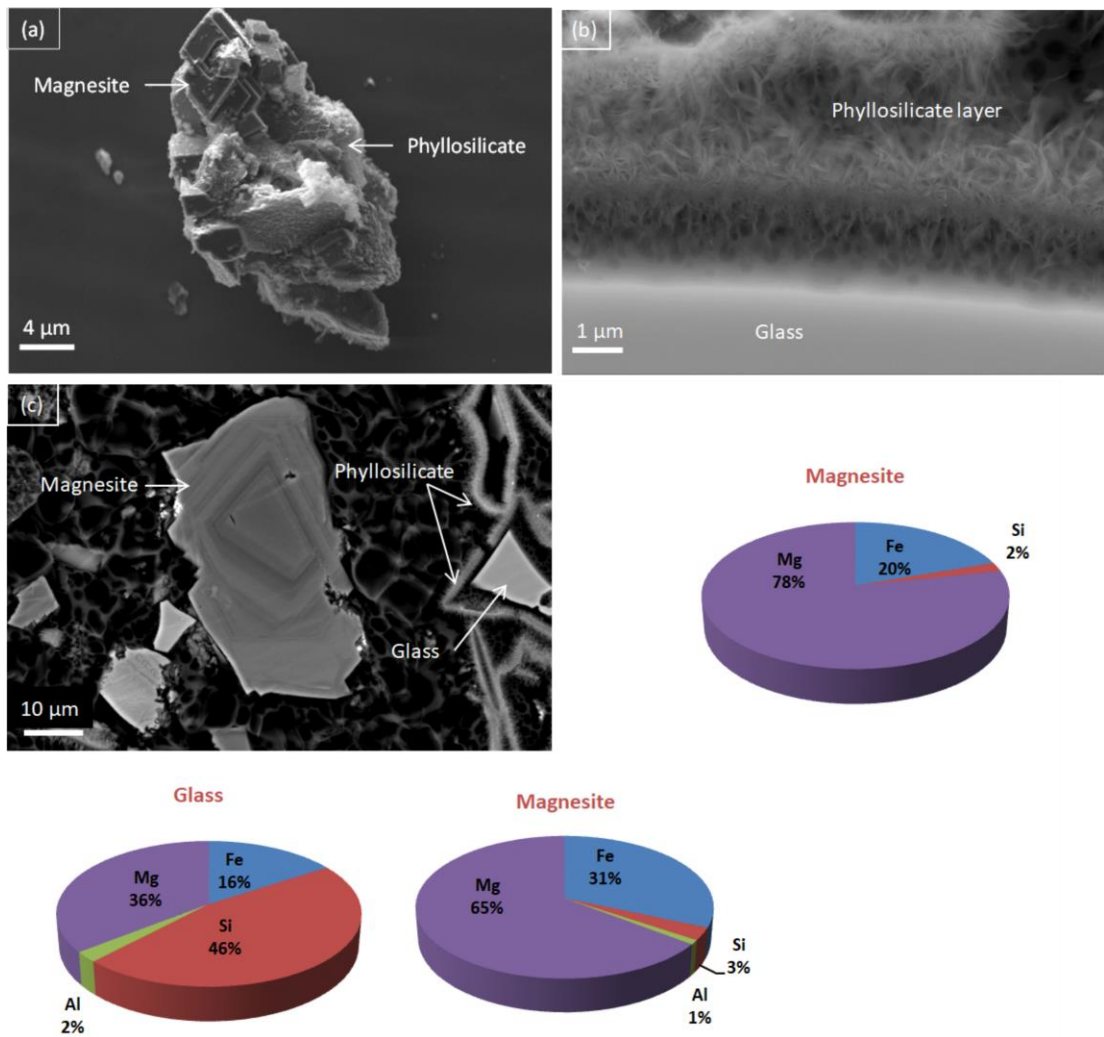
936 **SEM analysis on reaction products**

937 **S7.** SEM images of the ionically polished sections of experimental product at $T = 473\text{ K}$ and P
 938 $= 15\text{ MPa}$ showing large anhedral magnesite crystals grown around glass (gl) and olivine (ol).
 939 Secondary phyllosilicates (phy) layers around glass. (b) magnified image of yellow square
 940 marked on (a); (c) glass altered into magnesite; The chemical composition of phyllosilicate,
 941 magnesite, olivine and glass analyzed by SEM-EDX are shown in the pie charts.



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943 **S8.** SEM images of the ionically polished sections of experimental product at T = 523 K and P =
 944 30 MPa showing euhedral magnesite crystals and secondary phyllosilicates. (b) a magnified view
 945 of phyllosilicate (c) SEM image of a polished section of the products showing magnesite with
 946 zoning. The chemical composition obtained by SEM EDX analysis is shown in pie charts.

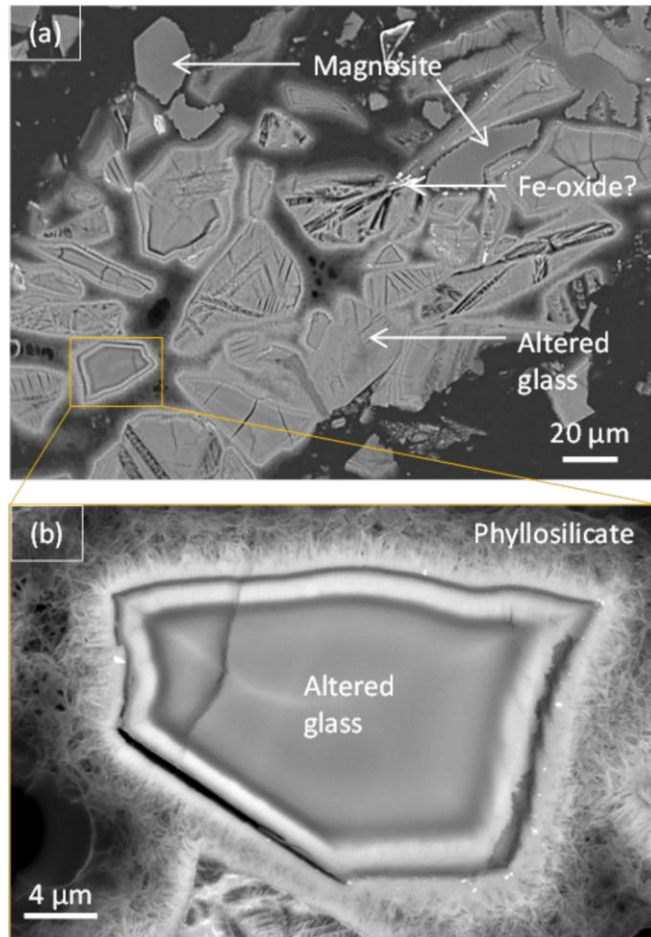


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950 S9. SEM images of the ionically polished sections of experimental product at T = 573 K and P =
951 30 MPa, showing anhedral magnesite formed around glass, and heavily altered glass with thick
952 layers of phyllosilicate.



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958 **S10. FIB –TEM analysis**

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

966

967 **S11. Calculation of maximum carbonation of mine tailings**

Fo88	molar mass		
(Mg _{1.76} ,Fe _{0.24}) ₂ SiO ₄	148.21 g/mol		
MgO _{1.76} + FeO _{0.24}	88.16		
Mg(0.8)Fe _{0.2} CO ₃	87.43 g/mol		
CO ₂	44 g/mol		<u>45 wt.% Fo88</u>
MgO _{1.76} + FeO _{0.24} +2CO ₂	176.16		79.272
Olivine + 2CO ₂	236.21 g/mol		106.2954
Ratio max carbonation	74.58%		74.58%
glass			
(Mg _{1.50} ,Fe _{0.50}) ₂ SiO ₃	126.45 g/mol		
MgO _{1.50} + FeO _{0.50}	82.4		
Mg(0.75)Fe _{0.25} CO ₃	92.125 g/mol		<u>55 wt.% glass</u>
CO ₂	44 g/mol		93.72
(Mg _{1.50} ,Fe _{0.50}) ₂ SiO ₃ +CO ₂	170.4		117.9475
GLASS + CO ₂	214.45 g/mol		79.46%
Ratio max carbonation	79.46%		
		Fo88+glass	<u>Average</u>
		MT composit	172.992
			224.2429
		Ratio max ca	<u>77.14%</u>

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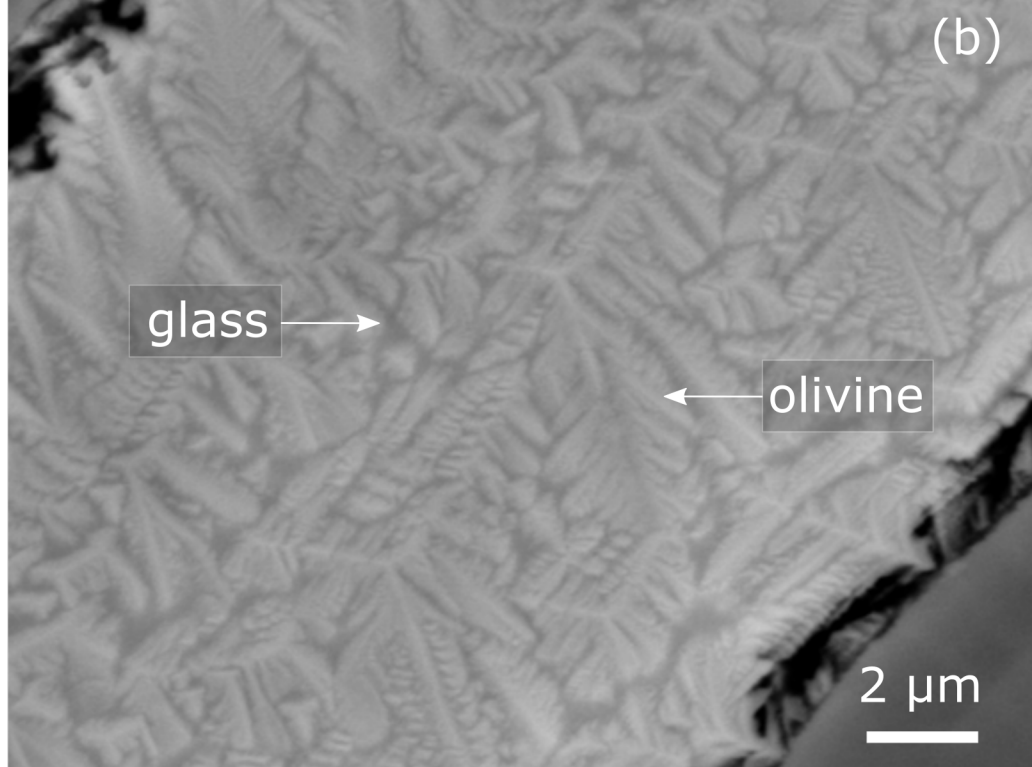
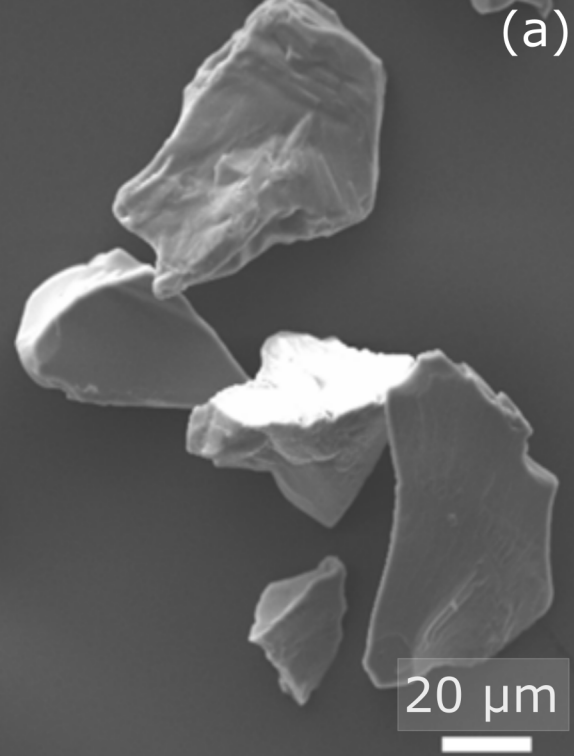
Figure 1. Powdered mine tailings observed under SEM (a) secondary electron image of powdered and cleaned sample used for the experiments. The grain surfaces are free of any adhered particles (b) angle selective back scattered image of a polished section of mine tailings showing the olivine crystals (white), embedded in glass (gray matrix) resulting a dendritic texture.

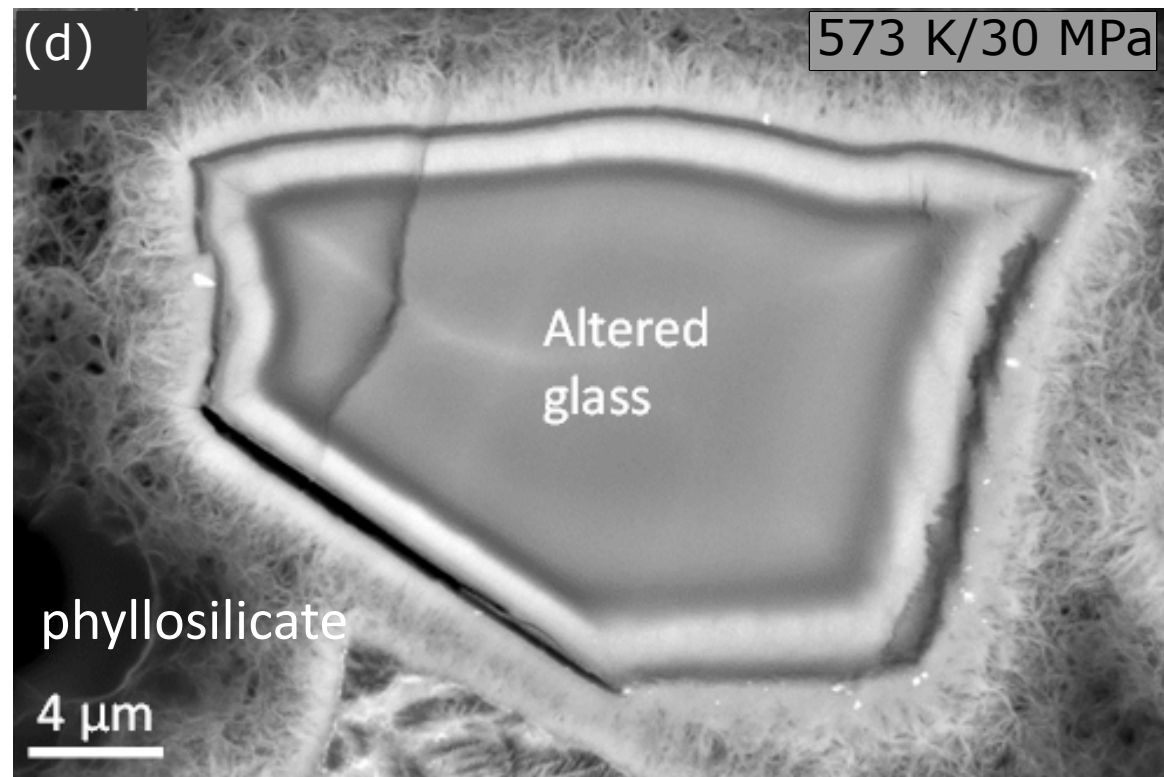
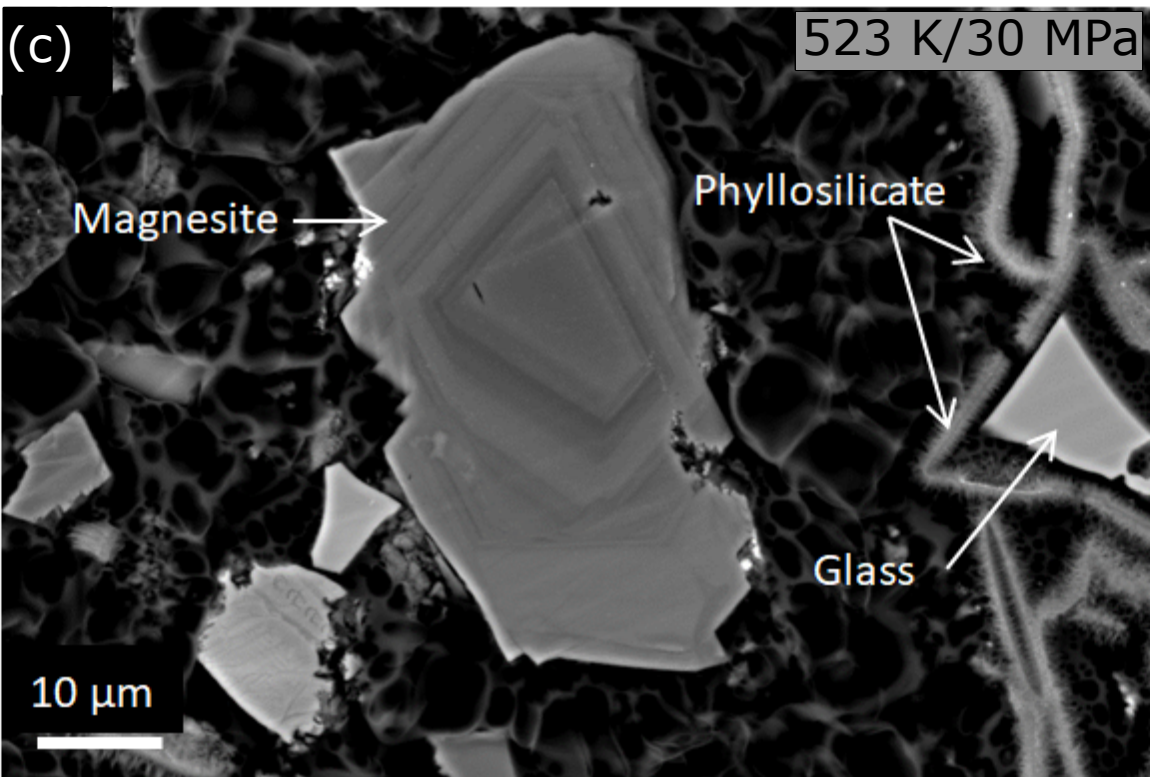
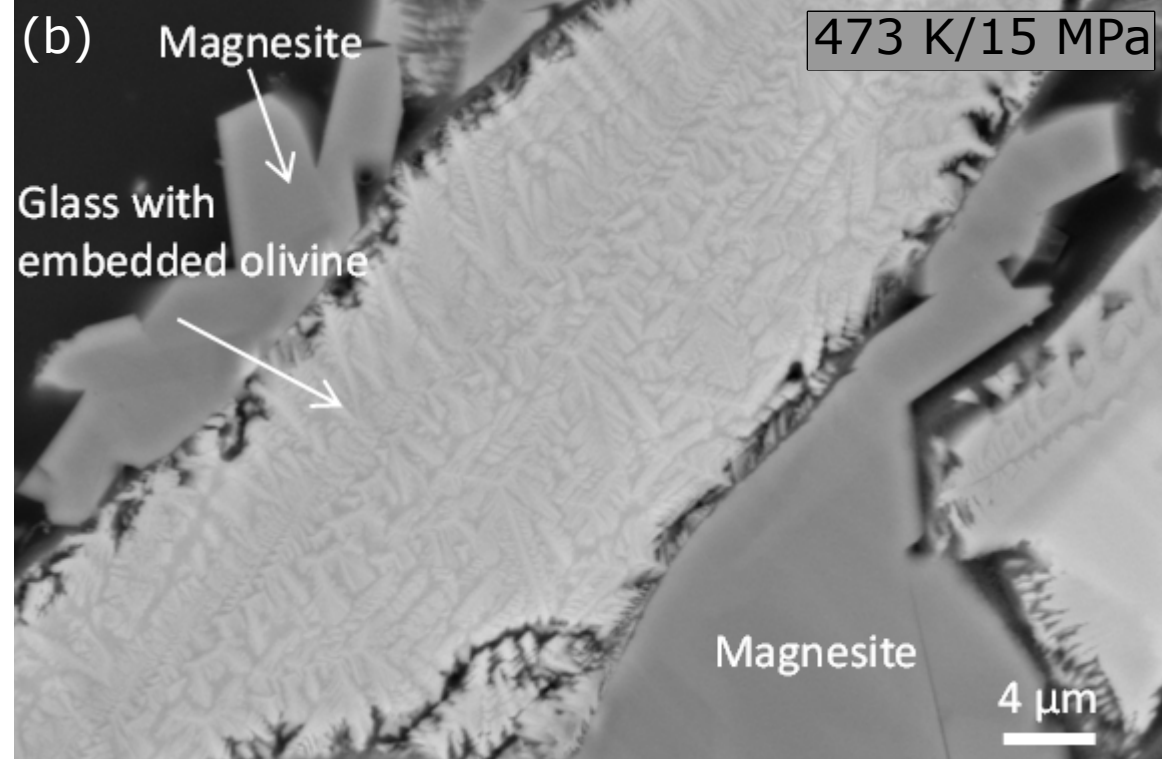
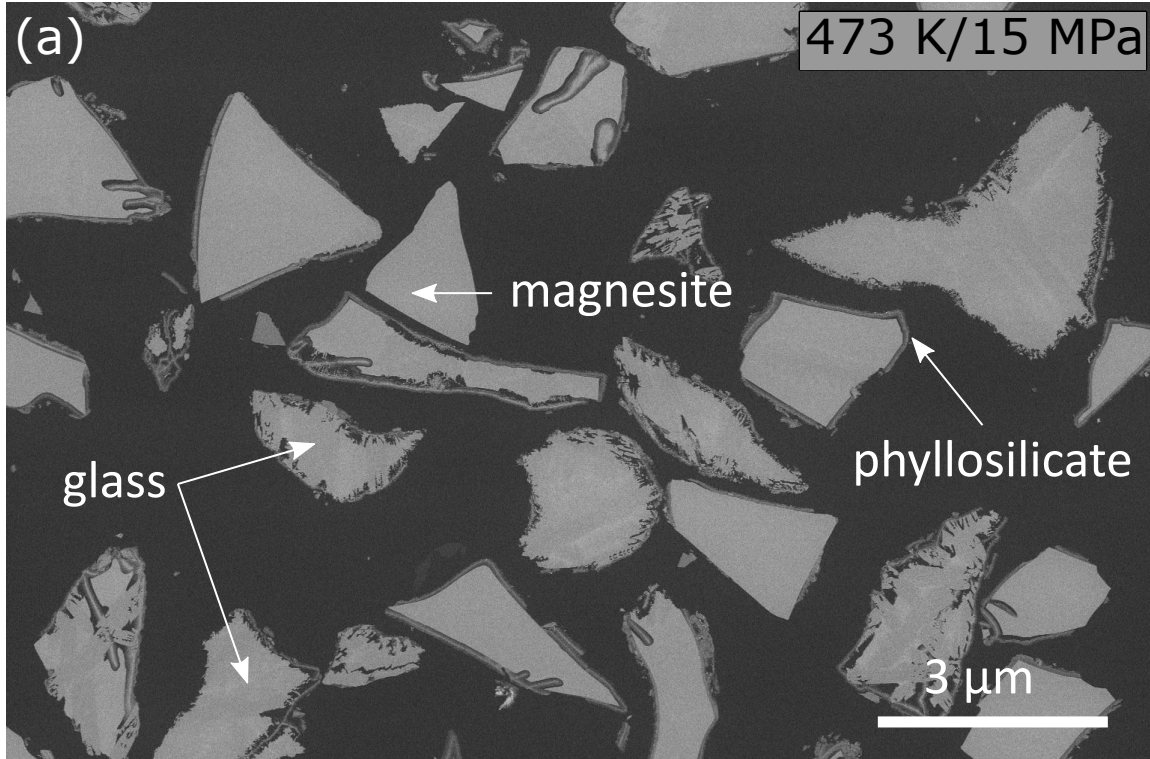
Figure 2. Mineralogical analysis of experimental run products (a) Element mapping (SEM) performed on a polished section the run product of experiment MT2 ($T = 523$ K and $P = 30$ MPa), showing formation of magnesite in large quantities (color coded by blue (Fe), green (Si) and red (Mg)). Magnesite crystals are shown in pink and initial silicate glass and traces of phyllosilicate is shown in green. A very small amount of iron oxide phases (not detectable through XRD) was observed only in this region of the sample and is marked in blue. (b) SEM secondary electron (In-lens detector) image of the same experimental run product taken on carbon coated powder showing euhedral grain of Fe-bearing magnesite (-as shown in SEM-EDX spectra) embedded in phyllosilicate. (c) X ray powder diffraction pattern of non-treated mine tailings sample and the run products of the three batch experiments, showing the progressive disappearance of olivine (O) peaks and the formation of magnesite (Mgs) during the reaction at high pressure and high temperature. The other secondary phases were phyllosilicates (Phy), and hematite (Hem). The peaks labeled (C) in the non-treated sample are the reflections of corundum which was added to the sample as the internal standard to quantify the fraction of glass (amorphous) in the initial non-reacted main tailings.

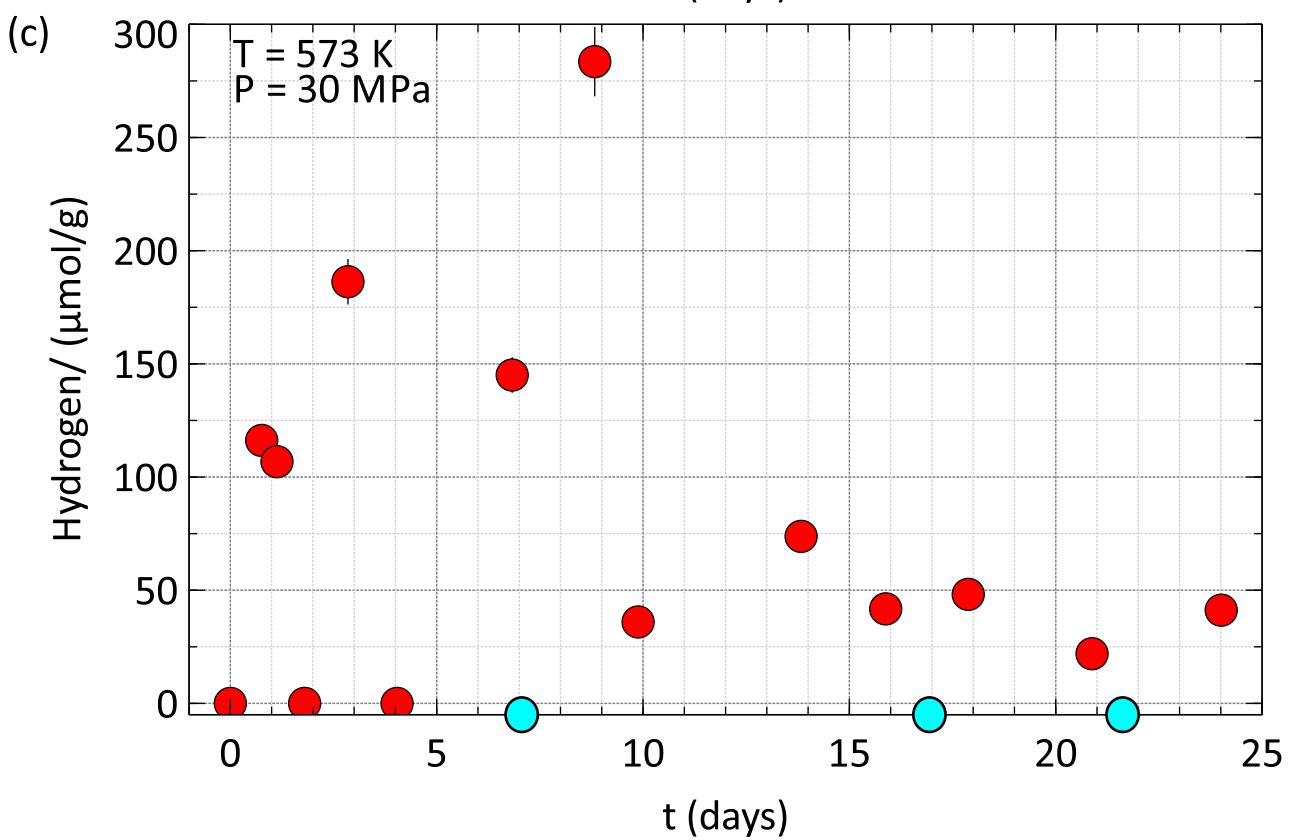
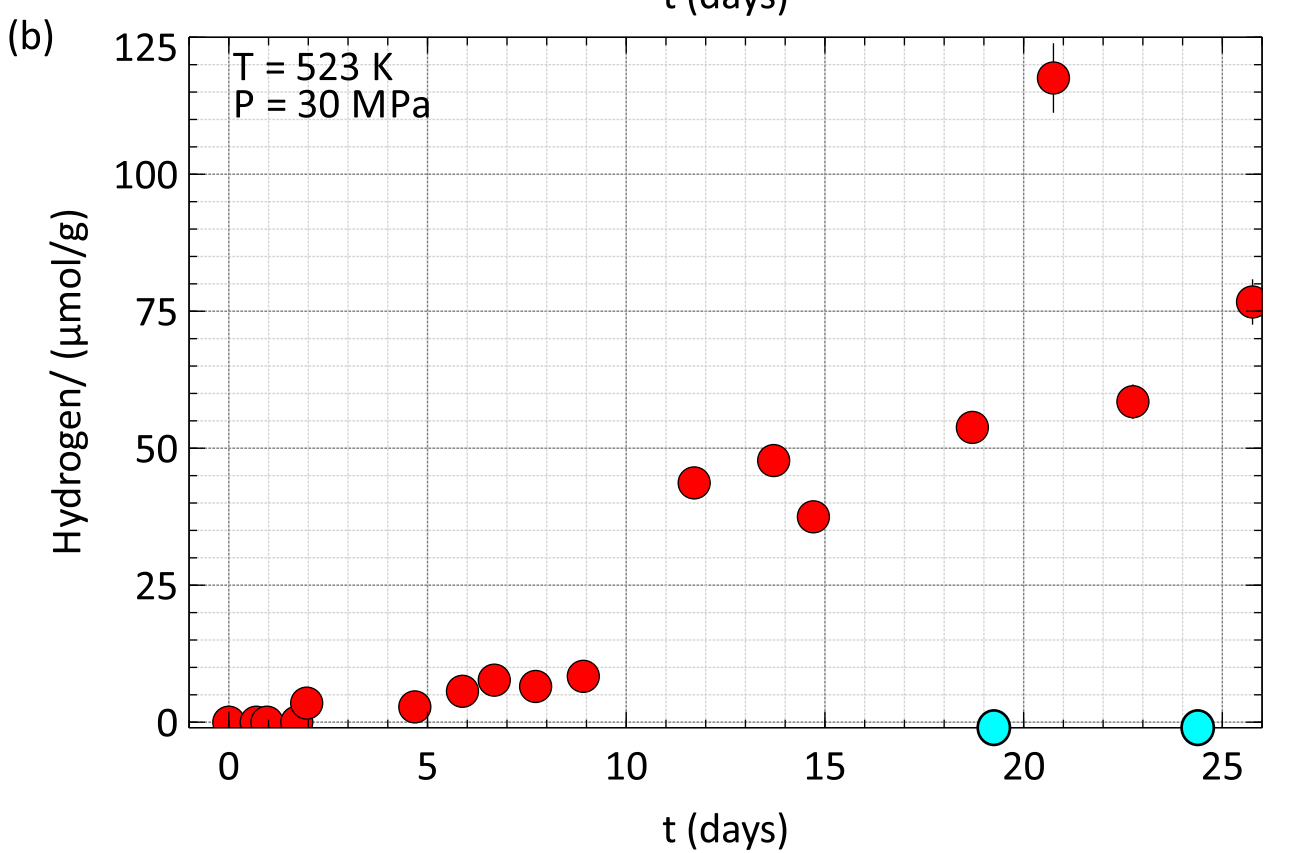
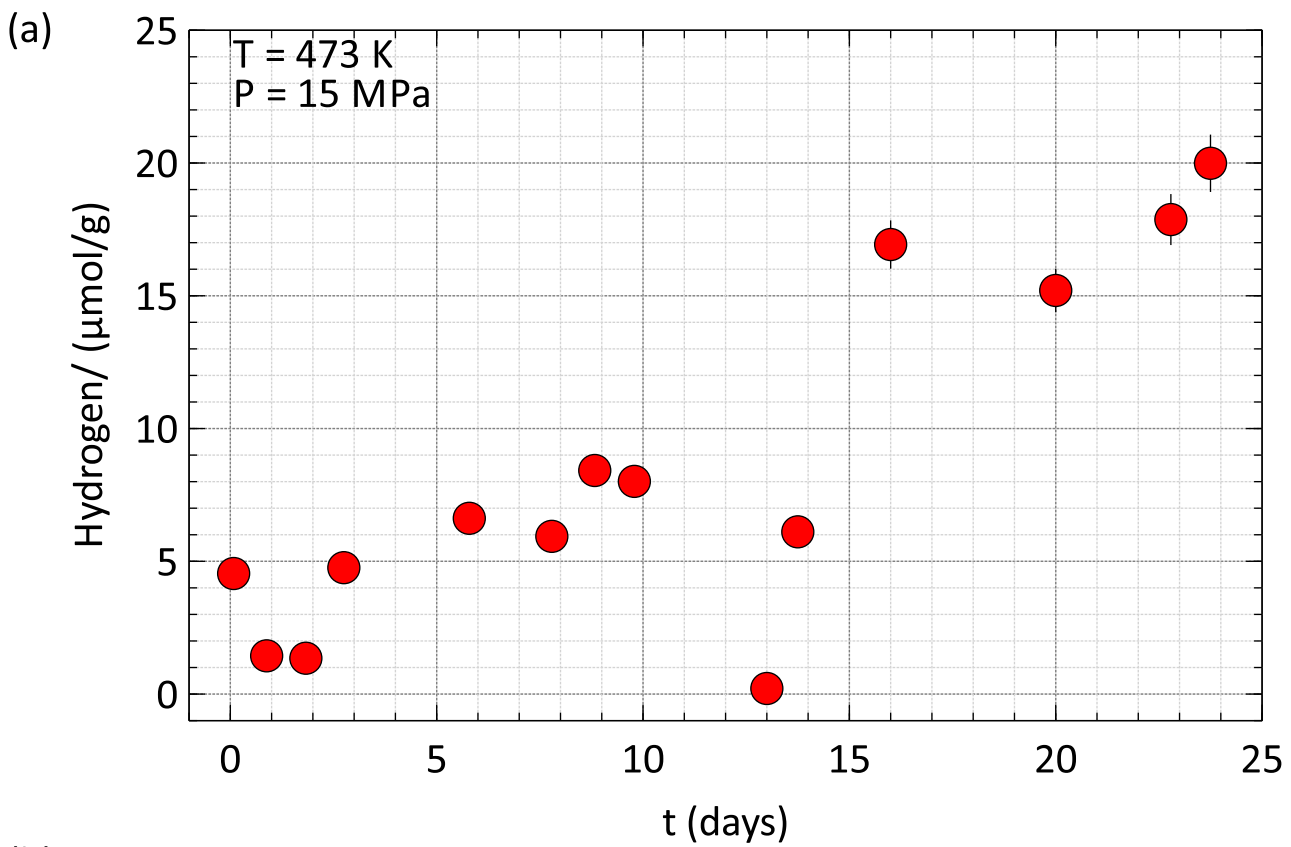
Figure 3. (a) SE image of the experimental run product at 473 K/15 MPa, showing some remaining glass, thin phyllosilicate layer formed around mine tailings and newly formed magnesite crystals; (b) a grain of mine tailing with olivine embedded in glass, which reacted to form anhedral magnesite crystals; (c) large magnesite crystals formed at 523 K/ 30 MPa showing Fe, Mg compositional zoning, and phyllosilicates which apparently detached from the original grains; (d) glass altered at 573 K/ 30 MPa forming a thick phyllosilicate layer.

Figure 4. Variations in the production of H₂, measured in the gas phase as a function of time (red points). The blue points represent blank experiments, which didn't yield any measurable concentrations of hydrogen. The error bars around the data points (smaller than the marker for most of them) represent a 5% uncertainty associated with the concentration measurements of hydrogen (H₂) by gas chromatography.

Figure 5: Quantities of magnesite precipitation and hydrogen production, obtained during the reaction of New Caledonian mine tailings, with CO₂-saturated water and as a function of temperature. The diagram emphasizes the competition between the two reactions. The shaded area indicates the temperature range at 30 MPa, recognized as the best conditions for the simultaneous carbonation and hydrogen production from mine tailings.







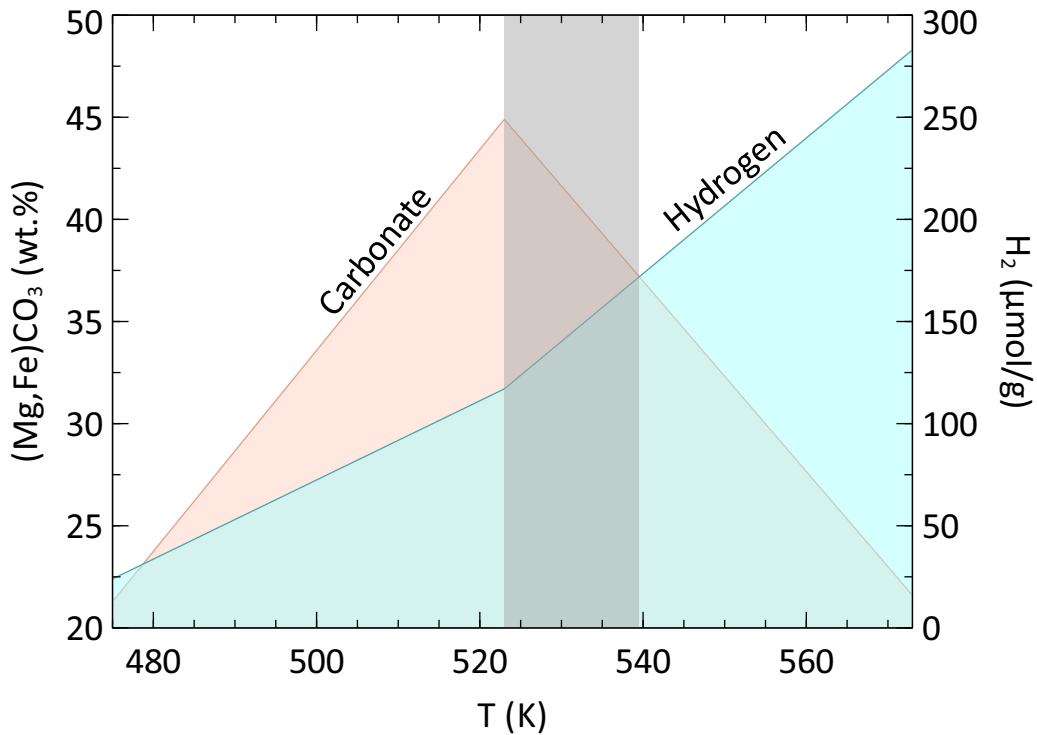


Table 1. The chemical composition of New Caledonian mine tailings, determined by electron probe micro analysis (EPMA) performed on crystalline olivine and glass, expressed in weight percent (wt.%) of corresponding oxide.

	Na ₂ O	MgO	SiO ₂	Al ₂ O ₃	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	FeO	MnO	CoO	NiO	Total	Mg# ^a
Olivine	0.05	47.27	40.88	0.07	0.01	0.11	0.04	0.02	11.67	0.12	0.05	0.38	100.68	0.88
Glass	0.04	23.94	55.22	3.81	0.01	0.48	0.06	1.68	14.23	0.9	0.01	0.01	100.39	0.75
Avg ^b	0.05	35.61	48.05	1.94	0.01	0.30	0.05	0.85	12.95	0.51	0.03	0.20	100.54	0.82

^aThe magnesium number; Mg# = Mg/(Mg+Fe)

^bAverage composition of mine tailings

Table 2. Summary of experimental conditions, pH of the solutions, carbonate yields, measured hydrogen and methane in each batch experiment.

	P(total) (MPa)	P(CO ₂) ^a (MPa)	T (K)	t (days)	Mine tailings (g)	Pure water (g)	water/rock ratio	Initial pH ^c	CO ₂ storage ^d (g/kg)	Hydrogen(max) measured by GC (g/kg) ^e	Methane(max) (g/kg) ^e
MT1	15	13.1	473	25	2.0	201	100	3.55	114.4	0.04	nd
MT2	30	26.4	523	25	1.7	170	100	3.65	320.5	0.24	0.02
MT4	30	28.2	573	24	1.7	170	100	3.94	118.5	0.57	0.05
MT2b (blank)	30	26.4	523	24	-	170	-	-	nd	nd	0.01
MT4b (blank)	30	28.2	573	24	-	170	-	-	nd	nd	0.06

^aCalculated for the given temperature and P(total) using the thermosolver software (Barnes and Koretsky, 2004)

^bSolid mass to solution volume ratio

^cpH at experimental conditions calculated using the CHESS geochemical code (van der Lee and De Windt, 2002)

^dgrams of molecular CO₂ trapped in 1 kg of mine tailings

^egrams of hydrogen (H₂), or methane (CH₄) produced per 1kg of mine tailings

nd = not detected in the gas chromatography analysis

Table 3. Production of hydrogen in each experiment estimated from FeO analysis. Reaction progress calculated based on the hydrogen production is also reported (Rx%).

Exp.	Wt (g)	T (K)	FeO wt%	FeO (mmol/g)	Δ FeO (mmol/g)*	Eq. H ₂ ^a (μ mol/g)	Eq. H ₂ (g/kg)	Rx%
MT ^b	2	-	9.39	1.31	0	no		
MT1	2	473	9.65 ^c	1.34	-0.03	-15	-0.03	-2.3
MT2	2	523	7.74	1.08	0.23	115	0.23	17.6
MT4	2	573	5.61	0.78	0.53	265	0.53	40.5

^aEquivalent hydrogen

^bMT refers to non-treated mine tailings

^cThis is an analytical error (see text), causing the successive negative values.

Table 4. Comparison of ex-situ CO₂ sequestration at 573K <T>423 K and P<30 MPa

Composition	d (μm)	P (MPa)	T (K)	t (h)	Solution	CO ₂ (g/kg) ^a	Reference
chrysotile (OK)	425-1000	12.4	428	1	1M NaCl, 0.64M NaHCO ₃	183.0	Bobicki et al., 2015
chrysotile (Pipe)	425-1000	12.4	428	1	1M NaCl, 0.64M NaHCO ₃	157.0	Bobicki et al., 2015
Olivine	20-80	15	423	336	supercritical CO ₂	261.0	Garcia et al.,2010
Olivine	40-63	15	473	600	CO ₂ -saturated water	114.4	This study_MT1
Olivine	40-63	30	523	600	CO ₂ -saturated water	320.5	This study_MT2
Olivine	40-63	30	573	576	CO ₂ -saturated water	118.5	This study_MT4

^aGrams of molecular CO₂ captured by one kg of starting material

Table 5. Comparison of hydrogen production by experiments conducted at 473 and 573 K.

Reference	Material	Solution	pH	T	t (h)	^b (H ₂ g/kg)
Malvoisin et al., 2013	^a CARBOF	water	6.9	473	69.2	0.01
Crouzet et al., 2017	FeO	0.05M acetic	3	473	72	5.34
This study	mine tailings	CO ₂ +water	3.6	473	66	0.07
Malvoisin et al., 2013	CARBOF	water	6.9	573	141	1.38
Crouzet et al., 2017	FeO	water	6	573	144	2.18
This study	mine tailings	CO ₂ +water	3.9	573	164	2.26

^aCARBOF=carbonated basic oxygen furnace steel slag

^bgrams of H₂ produced by 1 kg of FeO

Highlights

- New Caledonian mine tailings can be used for ex-situ CO₂ sequestration and H₂ production.
- Mg and Fe incorporation among the secondary phases play an important role.
- Maximum yields obtained at 523 K and 540 K at pCO₂=30 MPa.
- A novel method of valorization of Fe, Mg containing mine tailings.
- Cost effective method to treat CO₂ emissions and energy demands.