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Title: Atmospheric carbon sequestration in ultramafic mining residues and impacts on leachate water chemistry at the Dumont Nickel Project, Quebec, Canada

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Abstract: Passive carbon mineralization in ultramafic mining residues, which allows the sequestration of CO₂ through carbonate precipitation, is one of the options being considered to limit the accumulation of anthropogenic CO₂ in the atmosphere. The Dumont Nickel Project (DNP) will generate approximately 1.7 Gt of ultramafic mining residues over 33 years of production and the mine will release about 127,700 tonnes of CO₂ each year. Using two experimental cells filled with ultramafic waste rock (EC-1) and milling residues (EC-2), the impacts of carbon mineralization on leachate water quality were studied and the quantity of sequestered carbon was estimated. Hydrotalcite supergroup minerals, aragonite, artinite, nesquehonite, dypingite and hydromagnesite precipitated through atmospheric weathering, while the inorganic carbon content of the weathered mining waste increased from 0.1 wt% to 4.0 wt% which indicate active CO₂ sequestration. The leachate water, sampled at the bottom of the experimental cells, is characterized by an alkaline pH (~9.5), a high alkalinity (~90 to ~750 mg/L) and a high concentration of magnesium (~50 - ~750 mg/L), which is typical from weathering of ultramafic rocks in a system open to CO₂.

Since 2012, the chemical composition of the leachate water has evolved seasonally. These seasonal variations are best explained by: (1) climatic variations over the year and, (2) increased carbonate precipitation between May and July. Increased carbonate precipitation decreased the alkalinity and magnesium concentrations in the leachate water and produced pore waters which were undersaturated with respect to carbonate minerals such as artinite and hydromagnesite. Carbonate precipitation thus self-limits carbon sequestration through a negative feed-back loop. The carbon sequestration potential of the DNP residues is also influenced

by the hydrogeological properties of the residues. In cell EC-2, a high liquid/solid ratio, which limits carbonate precipitation, was maintained by the hydrogeological properties. Since 2011, an estimate of 13 kg of atmospheric CO₂ has been sequestered in the milling residues (EC-2), which corresponds to a mean rate of 1.4 (+/- 0.3) kgCO₂/tonne/year. Using this mean rate, the 15 Mt of tailings produced each year, during the planned 33 years of mining operation, could potentially sequester 21,000 tonnes of CO₂ per year by passive carbon mineralization, about 16% of the 127,700 tonnes of CO₂ annually emitted by the planned mining operation.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:

Data is in Supplementary Data appendices



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Québec, 28 April 2020

Dear Editor,

We are sorry for the long delay in submitting the revised version. The first author has moved to France and this has caused delays. I have taken over the role of corresponding author to complete the revisions. We thank the referees for their detailed comments which helped improve our paper significantly. We have made all required corrections except in a few minor cases where we disagree and explained our reasons. Our detailed response to the referees' comments are below.

Best regards,

A handwritten signature in black ink that reads "Georges Beaudoin".

Georges Beaudoin, géo.

Referee #1

Comments: 1. p. 1, line 34, and p. 3, lines 12-14. Over how many years will the anticipated 1.7 Gt of residues be produced? Over 33 years?

Yes, the anticipated 1.7Gt of mining residues should be produced over 33 years. The text has been modified in order to improve this section.

2.p. 2, lines 36-37. Consider separating these references according to which of the two processes (in situ versus ex situ) they relate to.

Difficult since some references refer to both (eg Olajire)

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4 3.p. 2, lines 45-47 and elsewhere in the manuscript. The notation for mineral
5 formulae ought to be tidied up a bit. The rules are a sometimes a bit strange,
6 but there's no need to use parentheses around the H₂O in hydrated carbonates or
7 hydrotalcite supergroup minerals. Also, a dot ought to be used rather than a
8 full stop for the crystallographic H₂O. Although the one interlayer CO₃ per
9 formula unit in pyroaurite polytypes is commonly given in parentheses (that's
10 all good as-is), the CO₃ group in the formulae of 1:1 Mg:CO₃ carbonates (such
11 as nesquehonite and lansfordite) is not given in parentheses.

12
13 Ok thanks for this correction.

14
15
16 4.p. 2, line 57. "by analyzing the carbon (C) isotope composition..." Is this
17 stable and/or radiocarbon?

18
19 Stable, corrected

20
21 5.p. 3, lines 15-16. Does "high partial pressure of CO₂" equate to pCO₂ above
22 atmospheric levels?

23
24 Yes, in this sentence high partial pressure of CO₂" equate to pCO₂ above
25 atmospheric levels. A full description of these tests are available in Assima
26 et al.

27
28 6.p. 4, line 17 or thereabouts, line 52 and line 57. I believe the Figure 3b
29 cited here should be Figure 1.

30
31 Yes, thanks

32
33 7.p. 4, line 26. There's no need to give the single nesosilicate group in the
34 olivine structure in parentheses. Missing '(' before the metal site in the
35 serpentine formula.

36
37 Ok

38
39 8.p. 4, lines 38-40. It might be worth describing the approximate difference in
40 grain size (or the precise ones if known) between tailings and waste rock for
41 readers who are less familiar with these materials.

42
43 A sentence has been added to help the reader to understand the differences
44 between cells EC1 and EC2 in the section describing each.

45
46 9.p. 4, line 59 and p. 5, line 9. I haven't come across the term "deshalming"
47 previously. It's not desliming or something similar is it? I think it would be
48 useful to add the definition for people who may not be familiar with the word.

49
50 Corrected to « desliming »

51
52 10. p. 5, line 49. A minor point: consider rephrasing this sentence to
53 something like "after the method of Oskierski et al." and then providing a

54
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4 citation for Wateq4f.
5 https://www.brr.cr.usgs.gov/projects/GWC_chemtherm/pubs/wq4fdoc.pdf
6

7 Revised accordingly.

8
9 11. p. 5, line 54. Consider using "white crusts of a mineral precipitate"
10 rather than "white crusts".
11

12 Done.

13
14 12. p. 6, line 53. Were the standards "analysed three times" rather than
15 "analysed after three analyses"?
16

17 Corrected to "after every set of 3 analyses"

18
19 13. p. 7, line 59. How is the uniformity coefficient defined?
20

21 The reader is referred to Kandji et al.

22
23 14. p. 8, line 10. Is this the volumetric water content (as labeled in Figure
24 4)?
25

26 Corrected to volumetric water

27
28 15. p. 8, lines 12-16. Was the H₂O liquid during the winter at such shallow
29 depths?
30

31 We have checked that the temperature measured by the same probe was circa 0 to
32 -1 C during these months such that H₂O must have been in the liquid state.
33

34
35 16. p. 8, lines 24-26. Were DI blanks run for comparison with rain water and
36 leachate water analyses? Not strictly necessary, but good to mention if so.
37

38 Analyses were carried in commercial laboratories following strict QA/QC
39 protocols including blanks.
40

41
42 17. p. 8, general comment. It's very cool to see the seasonality in your
43 leachate chemistry. The correlations are beautiful!
44

45 Thank you!

46
47 18. p. 8, line 54 to p. 9, line 9. Consider rephrasing this part to address
48 pH separately from the values for concentration in mg/L.
49

50 Done.

51
52 19. p. 9, line 35. "since 2011". For clarity, consider rephrasing as
53 something like "in the first 6 months of the experiment following set up in
54 2011".
55

56 Done.

57
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4 20. p. 9, line 37. With declining calcium concentrations? And leachate water
5 "generally remained over-saturated" since there are a few points below 0.
6

7 Added "generally".
8

9 21. p. 9, lines 56-60. A general comment that doesn't need to be addressed:
10 That's interesting that you see artinite. I've seen it (or amorphous phases of
11 similar composition) in relatively water limited conditions in the field, as
12 has Anna Harrison in the lab.
13

14 Thank you for the information.
15

16 22. p. 9, lines 56-60. Also very cool that you see brugnatellite. Do you see
17 the pyroaurite species more commonly at depth? I'm curious because Turvey et
18 al. (2018) IJGGC found a spatial relationship with hydrated Mg carbonates closer
19 to the surface and hydrotalcites containing lower mass proportions of CO2
20 dominating at depth.
21

22 This was not noted.
23

24 23. p. 10, line 22. Habit rather than habitus.
25

26 Corrected.
27

28 24. p. 10, lines 25-37. Can you elaborate on what you mean by "cracked"? Can
29 you be more specific about what you mean by "well-crystallized"? For instance,
30 do these minerals form larger, euhedral crystals or do they have a larger
31 crystallite size as determined from XRD data? Also, are you able to tell the
32 difference between aragonite and artinite in Figure 8d? There's a lot of useful
33 information in Figure 8. I think that annotating the subfigures to point out
34 the features you're describing, and labelling minerals with species
35 identifications, would be very helpful. With regard to Figure 8h, the scale here
36 is too large to be able to point out prokaryotes and there doesn't appear to be
37 a microbial mat preserved. (Were the samples preserved for biological microscopy
38 using glutaraldehyde in the field?) The large string-like features look like
39 fungal hyphae to me - those are commonly associated with ultramafic rocks in
40 weathering environments and they can be imaged fairly well without preservation.
41

42 "Cracked" removed as not shown in figures. Well-crystallized seems self-
43 explanatory- no changes, as figures show euhedral crystals. Artinite vs
44 aragonite: we cannot be more specific as stated in text. Modified to "potential
45 microbial mats or Fungal Hyphae".
46

47 25. p. 11, lines 19-20. 0.4 wt.% Corg seems a bit high for the detection
48 limit in light of the discussion in the next few sentences. Is this correct?
49

50 This is because the DL of Corg is much higher than that for Cinorg, see Gras et
51 al. 2017.
52

53 26. p. 11, lines 29-36. Although you mention it toward the end of the
54 manuscript (p. 20, lines 44-46), I think it's worth also mentioning that the
55 trends you see in Figure 10 could also be related to sample heterogeneity rather
56

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4 than seasonal dissolution and reprecipitation of carbonate minerals. I've seen
5 similar data sets when taking many cores from heterogeneous sediments and
6 tailings.

7
8 **Sample heterogeneity added.**

9
10 27. p. 12, line 56. Quantifying CO₂ uptake is tough to do and no method is
11 perfect. I think you've made a good contribution here and that you could replace
12 "to attempt to quantify" with "to estimate the amount of..."

13
14 **Thank you. Done.**

15
16 28. p. 13, line 27. I would recommend using "geomicrobial" or "biological"
17 rather than "organic" here.

18
19 **Modified to biological.**

20
21 29. p. 14, lines 22-32 and p. 19, lines 51-56. Do you see evidence for silica
22 precipitation or Mg-leached silicate grains?

23
24 **No. Despite looking for it.**

25
26 30. p. 14, lines 51-54. Good to cite Barnes and O'Neil (1969) here since
27 it's the original work that defined Types I and II waters.

28
29 **O'Neil and Barnes 1971 added, instead.**

30
31 31. p. 16, line 24. I like the discussion that follows about disequilibrium
32 and the ways to recognize it. I think it could flow even better if you (1)
33 mention here that it "could promote one of these three reactions over the others"
34 and (2) mention very briefly how this would affect the overall carbonation
35 reaction to tie this paragraph into the next one.

36
37 **Added "over the others". 2nd part, however will lead to repetition.**

38
39 32. p. 17, lines 9-13. That's quite cool. Do you see evidence for the same
40 return to equilibrium in your stable isotope data from your previously published
41 work? If so, it would be nice to tie that in here.

42
43 **Thank you. We do not have new δ¹³C to report.**

44
45 33. p. 18, line 19. It looks like nesquehonite is oversaturated for most of
46 the experiment from Figure 7. Are you referring to a specific time period? From
47 May to July? It's tricky to read this easily from the plots in Figure 7. Perhaps
48 pointing out the most important time periods using arrows or grey-shaded vertical
49 bands would help relate this discussion to Figure 7 more intuitively.

50
51 **The error was in the figure where wrong values are shown for the Y axis. Figure
52 7 modified with correct values.**

53
54
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4 34. p. 18, lines 44–56. The typical decomposition sequence is lansfordite -
5 nesquehonite - dypingite - hydromagnesite - magnesite, with all other phases
6 being metastable with respect to magnesite. Can you elaborate on what you mean
7 by hydrous carbonates evolving from lansfordite and nesquehonite (since these
8 are the most hydrated species)?
9

10 **Sequence of carbonate stability corrected as suggested by referee.**

11
12 35. p. 19, lines 9–13. Possibly. It's tough to say what the role of bacteria
13 might be since cell counts are commonly low in subaerial mine waste and tailings
14 impoundments. What I suspect are fungi in Figure 8h would help to decompose
15 organic material to potentially increase local concentrations of DIC. They would
16 also help to leach the rocks on a small scale. There's a good picture of fungal
17 hyphae on serpentinite in Power et al. (2009) Chem Geol for comparison (Figure
18 5).
19

20 **Very similar indeed. Changed to fungi, caption of Fig 8h also updated. Reference**
21 **to Power already included.**

22
23 36. p. 19, lines 22–26. These results relating to hydrotalcite supergroup
24 minerals have come out as Turvey et al. (2018) IJGGC.

25 **Turvey et al. (2018) was not known at time of submission. We can add, but Turvey**
26 **et al. 2015, 2017 already cited.**

27
28 37. p. 20, lines 4–9. In addition to the impacts of crystallization pressure
29 within pore spaces, could some of these fractures be artifacts of sample
30 preparation (e.g., thin sectioning)?
31

32 **NO because we embedded the samples in epoxy before fabrication of thin sections.**

33
34 38. p. 20, line 51 to p. 21, line 20. This is really nice.

35
36 **Thank you!**

37
38 39. p. 21, line 59 and start of p. 22. Did you also estimate the amount of
39 carbon sequestered in cell EC-1? If not, could you mention why (e.g., the grain
40 size was too coarse for coring, it was too heterogeneous, etc.)?
41

42 **This is explained at the start of section 5.3**

43
44 40. p. 23, lines 6–9. This is a really valuable conclusion. I would recommend
45 adding a little more to the very end of the manuscript. Describing possible ways
46 of optimizing the hydrological properties to enhance carbon sequestration would
47 kick it up a notch to really drive home the implications of your great study.
48

49 **The various factors affecting carbonation are discussed at length in previous**
50 **paragraphs. So we could rehash this in explaining control of water saturation,**
51 **etc. We fear this will appear repetitive. But this is really an engineering**
52 **optimization issue, somewhat outside the scope of the paper. If you request to**
53 **add this we will add a paragraph on optimization.**

54
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4 S.A. Wilson University of Alberta
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8 Reviewer #2: The manuscript entitled "Atmospheric carbon sequestration in
9 ultramafic mining residues and impacts on leachate water chemistry at the Dumont
10 Nickel Project, Quebec, Canada" discusses results from a carbonation experiment
11 run on waste rock and tailings of an ultramafic rock. The work is a follow-up
12 on a previous work by the same authors, with three additional authors (Gras et
13 al., 2017). While the previous paper introduced the experimental setup and
14 focused on isotope composition of the carbonates formed, the present manuscript
15 extends this work in a logical way by focusing on the composition of leachate
16 water from the experimental cells over several years. The manuscript is in
17 general well written and easy to read, and the topic fits the scope of the
18 journal well. Carbonation of ultramafic rock is an active research topic
19 presently, and research on carbonation of mine residues is particularly active.
20 Thus, I expect that the paper will attract significant attention. However, I
21 have some comments that should be taken into account, and recommend a moderate
22 revision. In the following, I list a major issue that I believe is quite
23 important to address, before I list some minor issues, including some spelling
24 mistakes. Since the line numbers on the manuscript don't actually match the
25 lines, I have used the line number nearest to the line I refer to.

26
27 Major issues I'm a bit concerned about the discussion of seasonal regimes in
28 section 5.1.2. On page 16, line 32 it is stated that carbonate precipitation
29 decreases magnesium and DIC concentrations in leachate water. This seems a bit
30 strange. Clearly, during evaporation the concentrations increase until reaching
31 saturation, and precipitation starts. I have a hard time understanding how this
32 can lead to undersaturated leachate water. I would rather expect that the
33 leachate water would then be close to saturation. Otherwise, the remaining water
34 after evaporation would have to be diluted with less concentrated leachate water
35 to produce the observed values. Similarly, when rainfall increases (page 17,
36 line 6) the concentration of magnesium and DIC increases in response to less
37 carbonate precipitation. This seems counterintuitive? Furthermore, (Page 17,
38 line 9) it is stated that the carbon mineralization reactions return to
39 equilibrium when rainfall increases. I would expect that the reactions are
40 closer to equilibrium when water stays a long time in the experimental cell in
41 dry periods than when lots of rain is entering continuously? Maybe all the fresh
42 rainwater might lead to redissolution of some carbonates? The potential effect
43 of such redissolution is not mentioned to any major extent in the manuscript,
44 and would be interesting to see discussed in a bit more depth. Needless to
45 say, I'm not sure I understand or believe the explanations the authors provide
46 in this section, and I thus recommend that they improve their arguments here.
47 This also has some impact on the conclusions.

48 We recognize the confusion created by this paragraph, which is in part
49 repetitive. We have deleted it and added a sentence to the 2nd paragraph of the
50 section:

51 Each year, the Mg concentrations and alkalinity values tend to be higher in the
52 spring (May and June) and fall (September to November), and lowest in the summer
53 (July and August). These trends are inverse with that of precipitations. It thus

54
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4 seems that Mg concentrations and alkalinity values (related to DIC) might be
5 controlled, at least in part, to dilution from rain and snowmelt water.
6
7
8
9

10
11
12 Minor issues :

13
14 Page 1, line 55: Either "... an estimated 13 ..." or "... an estimate of 13 ..."

15
16 Corrected to "an estimate of".
17

18 Page 2, line 32: In situ carbonation is also considered in ultramafic rock, with
19 the Oman Drilling Project probably being the largest project at the moment. As
20 for references for the in situ part, I would suggest some publication related
21 to the CarbFix project in Iceland for the mafic part and Kelemen et al. (2011)
22 for the ultramafic part.

23
24 Added Matter et al. (2009) for the CarbFix, and Kelemen and Matter (2008).
25

26 Page 3, line 4: Although these are indeed advantages, it would also be good to
27 mention some disadvantages, in order to be open about those.

28
29 Added a main disadvantage.
30

31 Page 4: All references to figure 3 are supposed to refer to figure 1.

32
33 Corrected.
34

35 Page 4, line 54: I assume that they intend to write "... rougher tails ..."

36
37 Corrected as suggested.
38

39 Page 4, line 56: Here, I assume that they intend to write "... run of mine ore
40 ..."

41
42 Yes corrected.
43

44 Page 9, line 35: Nesquehonite does not look under-saturated on figure 7.
45 Actually, the plotted data seems to be identical with the data for magnesite,
46 which leads me to assume that the authors have plotted the wrong data set for
47 nesquehonite.

48
49 Figure 7 modified as indicated in response to comments by S Wilson.
50

51 Page 9, line 56: As far as I know, there is no thermodynamic data for dypingite
52 available. I think it would be good to state this clearly somewhere, as it
53 otherwise seems a bit strange that nothing is written about dypingite in section
54 4.2.

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3
4 Not sure what to respond here. This section is the results description, and p.
5 9, L56 is the XRD results. Modelling is described later.
6
7

8 Page 11, line 29: Couldn't this also be caused by dissolution of carbonates
9 during weathering? After all, according to Ulven et al. (2017) there is almost
10 no carbonate left in the weathered part of the ultramafic rock.
11

12 The referee is mistaken, as this relates to the difficulty of measuring organic
13 carbon using Walkey-Black.
14

15 Page 12, line 4: I assume that "precipitation" here refers to rainfall, but it
16 would be good to distinguish more clearly between rain and carbonate
17 precipitation, since it might be confusing when two different concepts are
18 described by the same word.
19

20 Good point, changed to rain fall.
21

22 Page 12, line 46: I suggest rephrasing this sentence a bit. It seems the authors
23 are stating that this occurred in 2013 only, which seems a bit strange. Rather,
24 this is probably true for any year, but there is data for 2013 only. The
25 difference is minor, but important.
26

27 Not sure what is meant here. This line mentions the residence time of water in
28 cell EC-1. Then it discusses the flow rate in 2013, as measured, and compares
29 EC-1 and EC-2.
30

31 Page 13, eq (5): The equation is unbalanced, while the two previous are balanced.
32 I suggest having them all balanced. It's also unclear why the authors choose to
33 end up with nesquehonite in the general reactions.
34

35 Reaction corrected, nesquehonite simply used as an example. Added Harrison et
36 al., CG, 2019
37

38 Page 14, line 56: There seems to be a conjunction missing after the comma.
39

40 Indeed, corrected.
41

42 Page 15, line 17: Could such abrupt increases at first rainfall be caused by
43 formation of some easily dissolved minerals during dry periods, which would then
44 rapidly dissolve at first rainfall?
45

46 We have no evidence for that. We can only discuss the change in concentration,
47 and did not infer that dissolution involved only silicates from the waste
48 materials.
49

50 Page 16, line 57: had -> have
51

52 Done.
53

54 Page 18, line 44: dypinte -> dypingite
55

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2
3
4 Done.

5
6 Page 18, line 46: nesquesonihte -> nesquehonite

7
8 Done.

9
10 Page 20, lines 4-8: I suggest rephrasing this sentence a bit. The authors seem
11 to state that fracturing of the waste rock blocks actually occurred in the
12 experiment. Since there isn't any data in the results supporting such a
13 statement, I assume that the authors are intending to suggest the possibility
14 based on the references.

15
16 Replaced "blocks" with "fragments" as this is documented here.

17
18
19 Page 20, lines 51-59: It would be interesting to know if the layer of tailing
20 is flat, or whether water might pool in the middle. That would change the
21 hydrological setting significantly, and might cause the observed difference in
22 carbonate content.

23
24 Fig. 2e shows the surface is flat, but small irregularities ponded water. In
25 the following text we discuss the effect of the decreased thickness of materials
26 towards the edge of the cell.

27
28 Page 21, line 14: Again, I suggest distinguishing a bit clearer between
29 precipitation of rain and carbonate.

30
31 Done.

32
33 Page 21, line 16: Ulven et al. (2017) argued that sheltering from rain prevented
34 redissolution of the carbonates during rainfall. Could that be an alternative
35 explanation here?

36
37 Sentence to this effect added.

38
39 Page 21, line 29: I suggest rephrasing this sentence, since I'm pretty sure the
40 carbonate wasn't actually sequestered in the month of May 2015, but rather the
41 years from 2011 to May 2015.

42
43 Modified accordingly.

44
45 Page 21, line 47: How can 21 kt be one quarter of 127.7 kt? To me it seems more
46 like 16.4%. Furthermore, couldn't the tailing residues continue sequestering
47 several years in optimal conditions, and lead to sequestration of more CO2 than
48 estimated? If the rate is constant e.g. two years, then the first year 21 kt
49 would be sequestered, and then 42 kt all following years as the pile of material
50 is growing. One might have to consider optimal ways of spreading the tailing on
51 the ground or getting CO2 to percolate into the pile using pipes or pumps or
52 something, but it might be worth a try.

53
54 Indeed. Changed to 16%. Correct, we are describing annual rates.

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4 Page 22, line 46: alkanity -> alkalinity
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6 **Changed.**
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8 Figures 5, 6, 7: These multi-panel figures would be easier to read if there was
9 some sort background grid, e.g. vertical lines showing the start of each year.
10 As it is, I need to use a ruler if I want to compare data from the same time.
11

12 **Will do if requested, but this will make a mess of grid lines...**
13

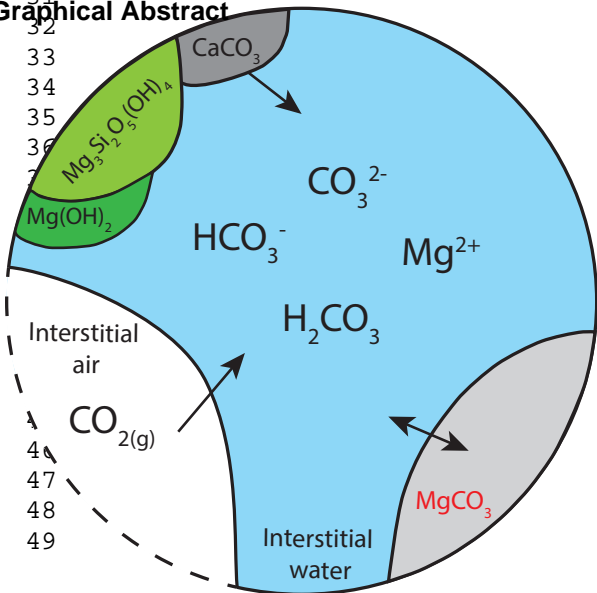
14 Figures 3, 7: The ticks on the horizontal top axes don't match those on the
15 bottom axes. That's inconvenient. The same is valid for the right vertical axis
16 in figure 7b).
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18 **Corrected**
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Graphical Abstract



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Highlights

- Passive carbon mineralization monitored in experimental ultramafic mine and milling waste
- Hydrotalcite supergroup minerals precipitated from atmospheric weathering, increasing C_{inorg} up to 4 wt.% CO_2
- Leachate water chemistry indicate weathering in steady state system open to atmospheric CO_2 .
- 1.4 kg CO_2 /tonne/year are captured from the atmosphere by passive carbon mineralization reactions

Atmospheric carbon sequestration in ultramafic mining residues and impacts on leachate water chemistry at the Dumont Nickel Project, Quebec, Canada

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Abstract

Passive carbon mineralization in ultramafic mining residues, which allows the sequestration of CO₂ through carbonate precipitation, is one of the options being considered to limit the accumulation of anthropogenic CO₂ in the atmosphere. The Dumont Nickel Project (DNP) will generate approximately 1.7 Gt of ultramafic mining residues [over 33 years of production](#) and the mine will release about 127,700 tonnes of CO₂ each year. Using two experimental cells filled with ultramafic waste rock (EC-1) and milling residues (EC-2), the impacts of carbon mineralization on leachate water quality were studied and the quantity of sequestered carbon was estimated. Hydrotalcite supergroup minerals, aragonite, artinite, nesquehonite, dypingite and hydromagnesite precipitated through atmospheric weathering, while the inorganic carbon content of the weathered mining waste increased from 0.1 wt% to 4.0 wt% which indicate active CO₂ sequestration. The leachate water, sampled at the bottom of the experimental cells, is characterized by an alkaline pH (~9.5), a high alkalinity (~90 to ~750 mg/L) and a high concentration of magnesium (~50 - ~750 mg/L), which is typical from weathering of ultramafic rocks in a system open to CO₂.

Since 2012, the chemical composition of the leachate water has evolved seasonally. These seasonal variations are best explained by: (1) climatic variations over the year and, (2) increased carbonate precipitation between May and July. Increased carbonate precipitation decreased the alkalinity and magnesium concentrations in the leachate water and produced pore waters which were undersaturated with respect to carbonate minerals such as artinite and hydromagnesite.

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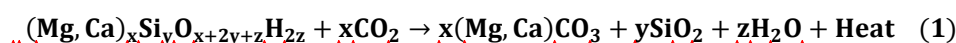
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Carbonate precipitation thus self-limits carbon sequestration through a negative feed-back loop. The carbon sequestration potential of the DNP residues is also influenced by the hydrogeological properties of the residues. In cell EC-2, a high liquid/solid ratio, which limits carbonate precipitation, was maintained by the hydrogeological properties. Since 2011, an estimated of 13 kg of atmospheric CO₂ has been sequestered in the milling residues (EC-2), which corresponds to a mean rate of 1.4 (+/- 0.3) kgCO₂/tonne/year. Using this mean rate, the 15 Mt of tailings produced each year, during the planned 33 years of mining operation, could potentially sequester 21,000 tonne of CO₂ per year by passive carbon mineralization, about one quarter 16% of the 127,700 tonnes of CO₂ annually emitted by the planned mining operation.

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1. Introduction

Anthropogenic CO₂ released into the atmosphere is considered a major driver of global climate change (IPCC, 2014). In order to limit accumulation of gaseous CO₂ in the atmosphere, several methods of carbon sequestration are envisaged including carbon mineralization (IPCC, 2005). As reviewed by Seifritz (1990), carbon mineralization technologies are derived from natural exothermic reactions, which occur spontaneously and trap CO₂ through carbonate precipitation (Berner and Kothavala, 2001; Gaillardet et al., 1999; Lackner et al., 1995). The general carbon mineralization reaction for silicate minerals such as serpentine is summarized in Reaction (1)-:



Carbon mineralization is attractive because no post-storage monitoring is necessary and carbon dioxide is sequestered over geological time scales. Two types of carbon mineralization are considered (Beaudoin et al., 2008; Gerdemann et al., 2007; Kelemen and Matter (2008); Matter et al. (2009); Olajire, 2013; Park and Fan, 2004; Pronost et al., 2011; Sanna et al., 2014; Sipilä et al., 2008; Teir et al., 2009):-:

(1) in-situ carbonation, wherein pure CO₂ is injected into subsurface mafic formations to form carbonate minerals, and

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55 [\(2\) ex-situ carbon mineralization, which uses mining or industrial residues as the](#)
56 [carbon sink.](#) ~~(2) ex situ carbon mineralization, which uses mining or industrial~~
57 ~~residues as the carbon sink.~~

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58 Natural weathering of ultramafic mining residues captures atmospheric CO₂ through
59 passive carbon mineralization. Carbonation rates of up to 1700 g C m⁻² y⁻¹, for example, have been
60 reported from historical and active mining sites. The main carbonate minerals precipitated in mining
61 residues are ~~p~~-Pyroaurite-3R [Mg₆Fe₂³⁺(CO₃)(OH)₁₆.4.4(H₂O)], nesquehonite [Mg(CO₃).3.3(H₂O)],
62 dypingite [Mg₅(CO₃)₄(OH)₂.5.4(H₂O)], hydromagnesite [Mg₅(CO₃)₄(OH)₂.4(H₂O)], and aragonite
63 [CaCO₃] (Beaudoin et al., 2008; Gras et al., 2017; Lechat et al., 2016; Oskierski et al., 2013; Power
64 et al., 2013a, 2013b; Pronost et al., 2012; Rollo and Jamieson, 2006; Turvey et al., 2017; Wilson et
65 al., 2011, 2006, 2014). Passive carbon mineralization has previously been studied by considering
66 mineralogical evolution and leachate water geochemistry (Assima et al., 2014a, 2013; Beinlich and
67 Austrheim, 2012; Harrison et al., 2017, 2013; Power et al., 2009; Rollo and Jamieson, 2006;
68 Zarandi et al., 2017a, 2017b, 2016), and by analysing the stable carbon (C) isotope (C¹³ and C¹²)
69 composition of dissolved inorganic carbon (DIC) and neo-formed carbonates (Beaudoin et al.,
70 2017, 2008; Gras et al., 2017; Harrison et al., 2016, 2013, Oskierski et al., 2013b, 2016, Wilson et
71 al., 2014, 2011, 2009). Ex-situ, passive carbon mineralization in mining residues has two main
72 advantages: (1) the mine wastes can be re-used for environmental benefit, and (2) CO₂ can be
73 directly sequestered from the atmosphere. Moreover, these processes can potentially lead to
74 developing carbon-neutral mines (Harrison et al., 2013; Hitch and Dipple, 2012; Mills et al., 2010;
75 Power et al., 2014). The main disadvantage is the slow rate of reaction, compared to ex-situ carbon
76 mineralization.

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77 The Dumont Nickel Project (DNP) of RNC Minerals (RNCM) is designed to produce 0.51
78 Gt of ultramafic waste rock and 1.18 Gt of milling (tailings) residues (Staples et al., 2013). The
79 carbon sequestration capacity of these future residues at high partial pressure of CO₂, and the effect
80 of mineralogy, water saturation, watering frequency, and temperature, have been well studied at the
81 laboratory scale (Assima et al., 2014a, 2014b, 2013, 2012, Kandji et al., 2017b, 2015; Plante et al.,
82 2014; Pronost et al., 2010; Zarandi et al., 2016, 2017a, 2017b). However, in order to develop useful
83 engineered solutions for carbon sequestration, and to properly estimate the carbon sequestration
84 capacity, more realistic field experiments are required (Olajire, 2013; Lechat et al., 2016; Gras et
85 al., 2017).

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86 Using two experimental cells, Gras et al. (2017) demonstrated that between the three
87 potential sources of CO₂, notably: (1) the atmosphere, (2) organic matter oxidation and (3)
88 carbonate dissolution, atmospheric CO₂ was the main source of sequestered carbon during natural
89 atmospheric weathering of the DNP residues. In addition, Gras et al. (2017) showed that dissolution
90 of atmospheric CO₂ in interstitial water was the first step which limited the carbon mineralization
91 capacity. However, additional factors can also limit the mineralization capacity. For example,
92 natural weathering of ultramafic rocks will change the geochemistry of meteoric water which
93 percolates through the mining residues (Rollo and Jamieson 2006; Beinlich et al., 2012; Oskierski et
94 al., 2016) and natural terrain (Bruni et al., 2002; Cipolli et al., 2004; Marques et al., 2008; Paukert
95 et al., 2012). Since changes in the water chemistry can affect carbonate precipitation, they may
96 therefore also impact the carbon sequestration potential of mine residues (Appelo and Postma,
97 2005).

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98 In this contribution, using two field experimental cells, EC-1 filled with mine waste, and
99 EC-2 which contains milling residue from the DNP, we report on changes in (1) leachate water
100 geochemistry, (2) waste mineralogy, and (3) carbon content. In addition, the effects of
101 hydrogeological properties and leachate water geochemistry on carbonate mineral precipitation are
102 investigated. Finally, the amount of atmospheric CO₂ trapped during atmospheric weathering of the
103 DNP residues is estimated.

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106 2. Geological setting

107 The DNP site is located near the town of Amos in north-western Québec (Figure 13a). The
108 deposit is hosted in a sill which had intruded into rock of the Superior province of the Canadian
109 Shield. Two distinct units are identified in the sill: (1) a mafic zone of gabbro which is overlain by
110 (2) an ultramafic zone formed by peridotite and dunite (Figure 13b) (Duke, 1986; Eckstrand, 1975;
111 Sciortino et al., 2015). The ultramafic zone, which contains a resource of 1.72 Mt of nickel ore, is
112 approximately 6.8 km long with an average thickness of 450 m. In the Dumont sill, nickel
113 enrichment of intercumulus minerals is a product of serpentinization (Duke, 1986; Sciortino et al.,
114 2015) which is a hydrothermal process involving water and heat which alters silicate minerals, such
115 as olivine [(Mg,Fe,Ni)₂(SiO₄)], to serpentine minerals [(Mg,Fe,Ni)₃Si₂O₅(OH)₄], as well as to
116 brucite [Mg(OH)₂] and magnetite [Fe²⁺Fe₂³⁺O₄]. The dunite protolith was composed of Ni-rich

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117 olivine with horizons rich in sulfide minerals. During serpentinization, the nickel was redistributed
118 in intercumulus pentlandite [(Fe,Ni)₉S₈], awaruite [Ni₃Fe] and heazlewoodite [Ni₃S₂] (Sciortino et
119 al., 2015). The main mineral assemblage in the dunite subzone consists of lizardite, magnetite,
120 brucite, and chlorite, with variable amounts of pentlandite, awaruite, and heazlewoodite (Sciortino
121 et al., 2015; Staples et al., 2013). The DNP is expected to generate approximately 1.7 Gt of
122 ultramafic mining residue of two types: (1) ~1.18 Gt of tailing residues issued from the
123 metallurgical processes, and (2) ~510 Mt of waste rocks (Staples et al., 2013).

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124 3. Materials and Methods

125 3.1 Experimental cells:

126 Near the planned DNP mining site near Amos, Quebec, two experimental cells were built
127 and instrumented in order to study weathering of the mine's ultramafic mining residues. Gras et al.
128 (2017) provide detailed descriptions of the experimental cells. The first cell (EC-1) was filled using
129 104 tonnes of waste rock from blasting of a dunite outcrop (Figure 1b). The grain size of waste
130 rock in EC-1 ranged from milimetric to pluricentrimetric blocs. The second cell (EC-2) contains
131 approximately 2.6 tonnes of milling residues containing the slimes, fluff and rougher tails (non-
132 magnetic) produced in a pilot plant. The run of mine ore, processed in the pilot plant, was taken
133 from four boreholes located in the dunite subzone (Figure 13b) (Staples et al., 2013). The pilot-plant
134 process consisted of two cycles of grinding, deshalmingdesliming, and flotation in a hydrocyclone
135 followed by magnetic separation. During the first cycle, the run of mine ore was crushed and
136 ground in wet media with the dispersant Calgon © (500 g/t) and potassium amyl xanthate (PAX)
137 (150 g/t) to 80% passing minus 150 µm, then the non-magnetic portion from the first cycle was
138 crushed and ground in wet media to 80% passing minus 74 µm for the second cycle of deshalking
139 and flotation.

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140 Within both experimental cells, gas sampling ports were installed in order to monitor CO₂
141 concentrations within the interstitial air (Gras et al., 2017). In addition, cell EC-2 contained a
142 Decagon 5TM probe, 4 cm below the tailings surface, to monitor changes in volumetric water
143 content and temperature. In November 2015, two additional Decagon 5TM probes were placed at
144 14 and 25 cm depths to measure changes in water content and temperature with depth. At the
145 bottom of cells EC-1 and EC-2, a geomembrane and a drain were installed to collect the leachate
146 water. Both drains were connected to tipping bucket rain gauges to log the flux of water at the
147 output of the cells. A weather station recorded solar radiation, temperature, wind speed and
148 direction, and a tipping bucket rain gauge measured rainfall.

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149 3.2 Leachate water analyses:

150 Leachate water is produced from infiltration of rain and meltwater through the mining
151 residues in experimental cells EC-1 and EC-2. The leachate was sampled twice a month between
152 July 2011 and November 2013, and then monthly from May 2014 to November 2015. The leachate
153 water pH was measured on site, while samples were collected in bottles which were sent to
154 Maxxam Analytical (QC, Canada) and to SGS Canada (ON, Canada) to measure major and minor
155 ions and metals (Al, Sb, As, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cu, Sn, Fe, Li, Mg, Mn, Mo, Hg, Ni, Pb,
156 K, Se, Si soluble in HNO₃, SO₄, Na, Sr, Tl, Ti, U, V, Zn), and total alkalinity, until 2015. The
157 geochemical model Phreeqc (Parkhurst et al., 1999) was used to calculate the saturation indices of
158 major carbonate minerals in the leachate water. Since the temperature of the leachate was not
159 measured, a temperature of 25°C was therefore used and [after the method of Oskierski et al. \(2016\)](#)
160 the thermodynamic equilibrium calculations were carried out using the Wateq4f database ([James
161 W. Ball and D. Kirk-Nordstrom, 1991](#) [Oskierski et al., 2016](#)).

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162 3.3 White crusts and core samples:

163 Within months of constructing the waste rock cell (EC-1), white crusts [of a mineral](#)
164 [precipitate](#) started to coat the surface of the rock fragments during atmospheric weathering. The
165 residues were sampled manually (Figure 2 a, b, c, d). White crusts [of a mineral precipitate](#) also
166 indurated the tailings surface near the edges of cell EC-2 which were also sampled (Figure 2 e, f, g,
167 h). Between 2012 and 2015, surface crusts were sampled 19 and 16 times in both EC-1 and EC-2,
168 respectively. In order to document the weathering processes acting on the residues, 7 cores, ranging
169 in length from 14 cm to 32 cm, were sampled from October 2013 to November 2015 in the center of
170 EC-2 using a steel tube (Gras et al., 2017). Additionally, two cores, 5 cm and 3 cm in length, were
171 sampled in October 2014 and May 2015. One core was sampled below a wooden access plank at the
172 edges of the cells and the other at the edges of the cell EC-2 (Figures 2 e and f) (Supplementary
173 information).

174 3.4 Mineralogical analysis

175 Crushed samples from cells EC-1 and EC-2 were analysed by XRD using a Siemens D5000
176 X-ray diffractometer (Cu-K α radiation). XRD patterns were collected with a scanning step of
177 1°/min (0.02° step size) over a 5-40° scattering angle range. The Jade computer program was used
178 to identify the mineral phases.

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179 A JEOL 840-A scanning electron microscope (SEM) at Université Laval, Québec, equipped
180 with an Avalon (PGT) energy-dispersive X-ray spectrometer (EDS), was used in order to describe
181 mineral habits and texture, and for mineral identification of the neo-formed phases.

182 Polished thin sections of white crusts from EC-1 and EC-2 were analyzed using a
183 CAMECA SX-100 Electron Probe Micro-Analyzer (EPMA) at Université Laval. The device is
184 equipped with 5 wavelength-dispersive spectrometers. Chemical analyses were performed using a
185 15 kV accelerating voltage with a 20 nA beam current, and a 10 µm beam size. Simple oxides
186 (GEO Standard Block of P and H Developments) and/or natural minerals (Mineral Standard Mount
187 MINM 2553, Astimex Scientific; Jarosewich et al., 1980) were used to calibrate the instrument for
188 chemical analyses.

189 3.5 Carbon content

190 The total carbon content was measured with an Eleetra CS 800 carbon and sulphur analyser
191 at Université Laval (Gras et al., 2017). High and low carbon contents were calibrated using,
192 respectively, AR 4018 (1.30 +/- 0.05 wt% C), and UB-N serpentine ANRT (0.106 +/- 0.08 wt% C).
193 The standards (Ar 4018 and UB-N serpentine) were analysed after every set of three analyses to test
194 reproducibility of the measurement over time, yielding a precision (1σ) of 0.2 wt% C and of 0.03
195 wt% C for the high and the low carbon contents, respectively.

196 The organic carbon content was measured using a modified Walkley Black method (Gras et
197 al., 2017; Walkley and Black, 1934) . Equation (2) below, from De Vos et al (2007)- was used to
198 calculate the organic carbon content:-

$$259 \quad \%C_{org} = M \times \frac{(V_1 - V_2) \times 0.3}{W} \times 1.32 \quad (2)$$

199 where M is the molarity of the reference Fe₂SO₄ solution, V₁ is the volume (mL) of Fe₂SO₄ needed
200 in a blank titration, V₂ is the volume (mL) of Fe₂SO₄ consumed in the sample titration, W is the
201 weight (g) of the sample and 1.32 is the correction factor (Chatterjee et al., 2009; Conyers et al.,
202 2011; De Vos et al., 2007).

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203 **4. Results**

204 **4.1 Field observations:**

205 The experimental cells are located near Amos, in north-western Quebec, in a continental
206 climate characterized by large differences in temperature between cold winters and warm summers.
207 The mean temperature and the mean solar radiation intensity between the years 2011 and 2016
208 varied respectively, from -18°C and 32 W/m² in winter to 17°C and 230 W/m² in summer (Table 1).
209 During summer, the rainfall events slightly decreased but intense rainfall events occurred frequently
210 (≥30 mm). The mean total annual precipitation (snow and rain) between 2011 and 2016 was 840
211 mm/yr. The recording of rainfall was sometimes disrupted by mechanical failure and was completed
212 using data from Environment Canada.

213 At the bottom of the cells, the leachate flow rate was recorded between April and November
214 using a typing bucket rain gauge. The logging was frequently disrupted due to weather. Figure 3
215 presents the flow rates recorded between May and August 2013, together with the rain events for
216 the year. In 2013, following a precipitation event of 25 mm in one day, the maximum flow rate in
217 EC-1 was ~2000 L/day whereas in EC-2 it was ~1400 L/day (Figure 3). The mean discharge
218 recorded between 2011 and 2015 ranged from 217 L/day to 546 L/day for EC-1 and from 111 L/day
219 to 241 L/day for EC-2 (Figure 3)

220 In cell EC-1, the grain size of the waste rock is heterogeneous and ranges from silt to pluri-
221 centimetric blocks whereas material from EC-2 is characterized by a D10 of 2.2 µm, a D80 of 119
222 µm and a uniformity coefficient (Cu=D10/D60) of 22 (Kandji et al., 2017) (Figure 2 a and e). The
223 mean porosity in cell EC-2 is 44% and the dry bulk density is 1242 kg/m³ +/- 55 kg/m³. Other
224 hydrogeological parameters for EC-1 and EC-2, presented in Gras et al. (2017), were estimated
225 from the literature (Aubertin et al., 1996; Lechat et al., 2016; Molson et al., 2008, 2005,
226 Peregoedova et al., 2014, 2012).

227 Figure 4 presents the evolution of the volumetric water content with depth in EC-2, with
228 total precipitation for the year 2016. During the winter, the water content just below the surface (~ 4
229 cm deep) was constant near 10% whereas at 14 cm and 25 cm depths the water content reached
230 30% and 40 %, respectively. In spring, the water content increased by 10 % throughout the cell and
231 fluctuated with rain events (Figure 4). Between 2011 and 2015, the average water content was ~25
232 % at 4 cm depth in cell EC-2.

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233 **4.2 Chemical evolution of the leachate water:**

234 Rainwater chemical analyses yielded a pH of 5.5 and contained trace amounts of Al (0.03
235 mg/L), Pb (0.001 mg/L) and Zn (0.03 mg/L). Between December and April, the interstitial waters
236 were frozen, thus chemical analyses on leachate water were performed only from May to
237 November. The leachate analyses from both cells revealed the same pattern of evolution, with a
238 transient phase after construction during the summer of 2011, followed by a regime characterized
239 by seasonal cycles (Figures 5 and 6).

240 In EC-1 during the first summer (2011), the magnesium concentration, alkalinity, and pH
241 increased from 6.5 to 110 mg/L (Mg), from 240 to 510 mg/L CaCO₃ (Alk) and from 8.17 to 8.81
242 (pH), respectively (Figure 5 a). During the same period, calcium and silica concentrations decreased
243 from 85 to 36 mg/L and from 7.8 to 3.3 mg/L, respectively (Figure 5 b). Since 2012, the magnesium
244 and silica concentrations, as well as the alkalinity and pH, varied in seasonal cycles from 125 to ~~750~~
245 180 mg/L (Mg), from 1.2 to 6.2 mg/L (Si), from 125 to ~~7050~~ mg/L CaCO₃ (Alk) and from 8.1 to 9.7
246 (pH), respectively. During these seasonal cycles, the magnesium concentration, pH and alkalinity
247 decreased while silica concentrations increased from May to August. From August to November the
248 trends were reversed (Figure 5 a,b). The calcium concentration generally decreases from year to
249 year but had the same seasonal variations as silica and ranged from 3.4 to 20 mg/L (Ca).

250 In EC-2, ~~with the exception of pH,~~ the concentrations of chemical elements were lower
251 than in EC-1 (Figure 6). Between July and November 2011, the magnesium concentration was
252 highly variable, with a minimum and maximum value of 70 and 120 mg/L, respectively.
253 Meanwhile, the alkalinity and pH increased from 45 to 180 mg/L CaCO₃ (Alk) and from 7.64 to
254 9.45 (pH), respectively (Figure 6 a), whereas calcium and silica concentrations decreased from 85
255 to 36 mg/L (Ca) and from 7.8 to 3.3 mg/L (Si), respectively (Figure 6 b). Between 2012 and 2015,
256 as in EC-1, the magnesium, silica and calcium concentrations, as well as alkalinity and pH, varied
257 seasonally between 50 and 140 mg/L (Mg), 0.9 to 7.2 mg/L (Ca), 0.67 to 2.7 mg/L (Si), 91 to 509
258 mg/L CaCO₃ (Alk) ~~and, with a rise in pH from~~ 8.93 to 10 ~~(pH),~~ respectively. While seasonal
259 variations were the same as in EC-1, the intensity of seasonal variations in magnesium
260 concentrations and alkalinity has decreased over the years in cell EC-2 (Figures 6 a,b).

261 In both experimental cells, potassium and sodium concentrations decreased from year to
262 year since 2011. Additionally, similar to silica, the potassium and sodium concentrations increased
263 each year between May and July then decreased until November (Figures 5 and 6). The potassium

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264 and sodium concentrations ranged from 4 to 2.3 mg/L (K) and from 13 to 2 mg/L (Na), respectively
265 in EC-1, and from 15 to 0.2 mg/L (K) and from 26 to 0.9 mg/L (Na) in EC-2 (Supplementary
266 information). The concentrations of other chemical components were near or below their detection
267 limits (Supplementary information). Finally, in both cells the amplitude of the seasonal cycles
268 seemed to decrease from year to year (Figures 5 and 6).

269 Thermodynamic equilibrium calculations revealed that carbonate saturation indices first
270 increased in 2011 and then evolved seasonally following pH and alkalinity. The calculations
271 suggest that magnesite, calcite and aragonite were over-saturated in leachate water, whereas
272 nesquehonite remained under-saturated in the first 6 months of the experiment following set up in
273 2011 since 2011 (Figure 7). The saturation indices of aragonite and calcite decreased over the years
274 with calcium concentrations, but the leachate water remained generally over-saturated with respect
275 to these minerals. Between May and July, saturation indices for hydromagnesite and artinite
276 decreased with the leachate becoming under-saturated whereas during the next three months,
277 saturation indices increased, with the leachate becoming over-saturated in November (Figure 7).
278 The thermodynamic equilibrium calculations also suggest that the partial pressure of CO₂ in the
279 leachate water was often below the atmospheric partial pressure, also fluctuating with seasonal
280 variations. However, the temperature of the leachate water was not measured which reduces
281 precision on the pCO₂ calculations.

282 **4.3 Mineralogical analysis:**

283 XRD analyses of weathered mining residues from both cells revealed the presence of
284 nesquehonite, dypingite, hydromagnesite, aragonite, artinite, and several minerals from the
285 hydrotalcite supergroup, including brugnatellite [Mg₆Fe³⁺(CO₃)(OH)_{13.4}(H₂O)], pyroaurite 3R, and
286 pyroaurite 2H [Mg₆Fe₂³⁺(CO₃)(OH)_{16.4}(H₂O)]. However, owing to the low modal abundance of the
287 carbonate minerals, XRD data did not allow an accurate identification of the hydrotalcite
288 supergroup minerals. Of the 19 samples analysed from EC-1, 10 contained hydromagnesite whereas
289 only one EC-2 sample contained hydromagnesite. Surface samples from EC-2 most often contained
290 dypingite. Well-crystalized, primary calcite [CaCO₃] was also found in rock fragments from EC-1
291 (Gras et al., 2017). Finally, in the first 3 centimeters of the core samples at the center of cell EC-2, a
292 decrease in intensity or an absence of brucite peaks was observed in the XRD patterns of the
293 weathered samples.

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294 The SEM observations of weathered samples from EC-1 and EC-2 revealed the texture and
295 habit of the precipitated carbonates (Figure 8). The weathered surfaces of samples from the waste
296 rock cell (EC-1) were entirely (Figure 8 a) to partially (Figure 8 b) covered by carbonate minerals
297 with a lamellar texture similar to the habitus of hydromagnesite (Figure 8 c). On the surface of
298 several samples, at the grain surfaces, depressions were filled with carbonate minerals ~~which~~
299 ~~appeared cracked~~, whereas on the top of the grains some well-crystallized lamellar minerals were
300 observed. Well-crystallized carbonate minerals with the typical texture of aragonite or artinite have
301 also been observed on samples from EC-1 (Figure 8 d). At the surface of EC-2, carbonate minerals
302 cement small grains of tailings (Figure 8 e). Flaky carbonate minerals covered by well-crystallized
303 needle-like minerals were observed on the same serpentine grains (Figure 8 f). Additionally, several
304 crystal sizes of nesquehonite were observed on the same samples which indicate repeated
305 precipitation phases (Figure 8 g). Finally, some samples from EC-2 ~~were characterized by~~
306 ~~intergrowths of contain potential~~ microbial mats of fungal hyphae intertwined with carbonate
307 minerals (Figure 8 h).

308 Using samples from cells EC-1 and EC-2, thin sections were impregnated with epoxy under
309 vacuum, in order to preserve the carbonate-matrix interface. The carbonate crusts from EC-2
310 samples were too thin for EPMA analysis. Back Scattered Electron (BSE) imaging of the thin
311 sections from EC-1 revealed different patterns of carbonate coating. The carbonate minerals were
312 observed as: (1) thin layers on the serpentine substrate separated from lamellar minerals by a
313 fracture (Figure 9 a), (2) within fractures cemented by carbonate with mining residue fragments
314 (Figure 9 b) or (3) in complex fractures filled by carbonates and with brucite (Figure 9 c). The
315 minerals at the carbonate-matrix interface had oxygen, magnesium and silica concentrations ranging
316 respectively from 61.9 to 13.8 wt% (O), from 47.1 to 6.7 wt % (Mg) and from the detection limits
317 to 21 wt% (Si). Nickel, calcium and aluminum never exceeded 2.3 wt % whereas the iron was
318 commonly lower than 2 wt% , reading 8 wt% in one grain.

319 **4.4 Evolution of the carbon content:**

320 The unweathered mining residues within the experimental cell EC-1 were characterized by
321 a total carbon content of 0.13 wt%, whereas the white crusts, which do not contain primary calcite,
322 had a total carbon content ranging from 0.3 wt% to 4.4 wt% C_{tot} (Gras et al., 2017). In cell EC-1, no
323 evidence of organic carbon was observed, and therefore the total carbon content is equivalent to the
324 inorganic carbon content. In contrast, in cell EC-2, spruce needles and leaf fragments were found at
325 the surface (Figure 2 f) thus the organic carbon content was measured in order to compute the

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326 inorganic carbon content. In several samples the organic carbon content was near the detection limit
327 (0.4 wt% C_{org}) (Conyers et al., 2011). Therefore, in samples with a carbon content below 0.4 %C_{org},
328 the total carbon was considered to be inorganic carbon (Gras et al., 2017). In EC-2, the unweathered
329 residues had a total carbon content of 0.08 wt%. The crusts sampled at the edge of the cell were
330 characterized by an inorganic carbon content ranging from 0.1 wt%C_{inorg} to 4.0 wt%C_{inorg} (Gras et
331 al., 2017). The samples from the first few centimeters of core samples, at the center of cell EC-2,
332 yielded inorganic carbon contents lower than the carbon content of the unweathered mining
333 residues (Figure 10). This is likely a consequence of measurement errors related to the Walkey-
334 Black method or sample heterogeneity. Moreover, the inorganic carbon content changed according
335 to the month of sampling. Below the first centimeter of depth, the inorganic carbon content
336 decreased quickly from 1 cm to 3 cm depth. Between 2014 and 2015, the inorganic carbon content
337 ranged from 0.15 wt% to 0.43 wt% and was higher in July than in May or October/November. From
338 below 3 cm depth to the bottom of cell EC-2, the inorganic carbon content was constant near
339 0.2 wt% (Gras et al., 2017) (Figure 10). Figure 11 presents the inorganic carbon content measured
340 at the surface of EC-2 since 2011, and a cross-section of cell EC-2 with the spatial distribution of
341 the inorganic carbon content measured in May 2015. The contours were drawn using linear
342 interpolation between the core samples. The mining residues under the wood plank, at the edges of
343 cell EC-2, (Figure 2 g) had an average inorganic carbon content of 1.08 wt% whereas at the edges
344 of the cell in May 2015, the inorganic carbon content decreased from 0.5 wt % at the surface, to 0.3
345 wt% at a depth of 10 cm.

346 5. DISCUSSION

347 Since construction of the experimental cells during the summer of 2011, the mining
348 residues underwent atmospheric weathering. Previous work demonstrated that passive carbon
349 mineralization had indeed induced atmospheric carbon sequestration in the DNP residues (Gras et
350 al., 2017). The main parameters controlling the extent of mineral carbonation include characteristics
351 inherent to the residues such as the mineral composition, surface area, porosity and permeability.
352 Other parameters depend on the environment, such as ~~precipitation-rain fall~~ frequency, temperature,
353 and relative humidity (Assima et al., 2014c, 2013, 2012; Awoh et al., 2014; Bea et al., 2012;
354 Harrison et al., 2015; Kandji et al., 2017a, 2017b; Pronost et al., 2011; Wilson et al., 2014; Zarandi
355 et al., 2017b, 2016). Both experimental cells (EC-1 and EC-2) were filled with ultramafic mining
356 residues from the same nickel deposit. Mining residues in EC-1 and EC-2 therefore had a similar
357 initial mineralogy (Figure 3a-b) where the main minerals were chrysotile, lizardite, brucite, chlorite
358 and magnetite, whereas calcite was found in minor amounts in the waste rock residues (Pronost et

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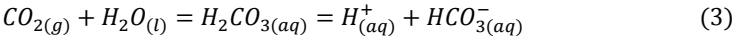
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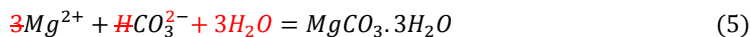
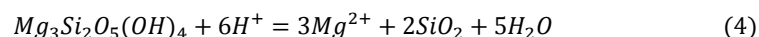
al., 2010; 2012; Staples et al., 2013; Gras et al. 2017). The brucite content in the tailings residues of cell EC-2, was approximately 10.2 wt% (Assima et al., 2013). During 4 years of monitored weathering, the residues were submitted to the same conditions of precipitation, temperature and relative humidity variations. However, the hydrogeological characteristics of the mining residues (porosity, water content, tortuosity, permeability), which are specific to each cell, control the flows of gas and water. Cell EC-1 has hydrogeological properties analogous to a heterogeneous gravel-silt, whereas in cell EC-2 the porous medium is similar to that of a silty-clay (Figure 2). On the other hand, the cells contained respectively, approximately 104 tonnes (EC-1) and 5 tonnes (EC-2) of residues and the surface area exposed to rainwater was greater for cell EC-1 (~35 m²) than for EC-2 (~19 m²). As a result, the cell thicknesses are about 2 meters and 35 centimeters, respectively, for EC-1 and EC-2. The liquid-solid ratio and thus also the water content were higher in EC-2 (Figure 4) than in EC-1 (Gras et al., 2017). The flow rates measured at the bottom of the cells thus depended on the hydrogeological properties of each cell. After a rain event, an abrupt increase of the flow rate was recorded in both cells (Figure 4). Counter-intuitively to what the hydrogeological properties would suggest, in cell EC-1 the flow rate decreased slowly in the recession curve (Figure 3) whereas in EC-2 the flow rate decreased more quickly after a rain event. This is best explained by the small amount of mining residues within EC-2. Despite a porous medium similar to a silty-clay, the smaller thickness in EC-2 (35 cm) resulted in a short residence time for water. In EC-1, the residence time of water was longer but did not exceed a few days (Figure 3). In 2013, the flow rate measured at the bottom of EC-1 was higher than in EC-2 which was most likely due to the difference in the surface area exposed to rain. Physical property differences between the two cells may influence the carbon mineralization reactions and, therefore, the carbon sequestration capacity. In the following sections, the observed impacts of atmospheric weathering on leachate water geochemistry will be used to discuss the evolution of carbon mineralization over time and to ~~attempt to quantify estimate the amount of the~~ atmospheric CO₂ sequestered in the cells.

5.1 Impacts of atmospheric weathering on leachate geochemistry.

In cells EC-1 and EC-2, rainwater in equilibrium with atmospheric CO₂ infiltrates the mining residues and dissolves the magnesium (Mg²⁺) from minerals such as brucite or serpentine. The Mg²⁺_(aq) released into leachate water reacts with interstitial water carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) ions to form carbonate minerals (Sanna et al., 2014; Harrison et al., 2019), following reactions 3-5 below:



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390 Dissolution reactions (3 and 4) and carbonate precipitation (5) are controlled by temperature, pH
 391 and solution chemistry, and may also be affected by organic-biological processes (McCutcheon et
 392 al., 2016; Power et al., 2013a, 2016, 2010, 2009). In the experimental cells, reactions 3, 4 and 5
 393 occur simultaneously such that the leachate waters collected at the bottom of both cells reflect the
 394 equilibrium between these reactions at the times of sampling. From 2011 to 2015, and despite
 395 differences in physical properties between the two cells, two regimes can be recognized for leachate
 396 water chemistry (Figures 5 and 6). First, a transitional regime in 2011 during which the pH,
 397 alkalinity and magnesium concentrations increase in the leachate water whereas silica, calcium,
 398 potassium and sodium concentrations decrease. In the second regime, starting in 2012, the pH,
 399 alkalinity, Mg, Si, Ca, Na and K concentrations in leachate water show seasonal variations, while
 400 the other metal concentrations are stable or below detection (Supporting information). The greater
 401 amount of mining residues and the larger surface area of EC-1 to collect rain, as well as its
 402 hydrogeological parameters which are more favourable to water infiltration compared to that of cell
 403 EC-2, could explain the higher concentrations observed in cell EC-1 (Figures 5 and 6). However,
 404 the concentrations normalized to the volume of mining residues demonstrate that the release rates of
 405 different components in EC-1 were lower than in EC-2 (Kandji et al., 2017). The contrast in release
 406 rates between both cells may be explained by (1) the finer grain-size and thus a higher specific
 407 surface in cell EC-2, and (2) the high liquid-solid ratio in EC-2 (Plante et al., 2014, Kandji et al.,
 408 2017). Despite these differences, the same processes appear to control the evolution of the leachate
 409 water chemistry in both cells (Figures 5 and 6).

410 5.1.1 Transitional regime

411 In July 2011, atmospheric weathering of the mining residues began with acidic meteoric
 412 water (pH ~ 5.5) infiltrating the mining residues and dissolving serpentine minerals, brucite and
 413 minor amounts of diopside, albite, biotite and calcite (Staples et al., 2013; Pronost et al., 2012,
 414 Kandji et al., 2017). The increase of Mg concentration in leachate water was congruent with the
 415 dissolution of serpentine minerals, brucite and minor silicate minerals. Dissolution of brucite is
 416 further suggested by a decrease of intensity or absence of the XRD peaks of brucite in weathered
 417 EC-2 samples. Concurrent to dissolution, H⁺ was consumed through weathering, which caused pH
 418 and alkalinity increases in leachate water (Figures 5 and 6) (Kandji et al., 2017b; Lechat et al.,

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419 | 2016; Ulven et al., 2017). Concentrations of Si, Ca, Na or K in leachate water indicate active
420 | dissolution of serpentine minerals and silicate minerals such as diopside, albite or biotite. On the
421 | other hand, a decrease of Si and other metal concentrations between July and November 2011
422 | suggests a lower dissolution rate of serpentine and silicate minerals during this period, which is
423 | consistent with the pH increase and a decrease of the abundance of these minerals (Figures 5 and 6).
424 | Additionally, the increasing pH may cause incongruent dissolution of serpentine minerals, and a
425 | preferential release of Mg over Si (Pokrovsky and Schott, 2000), which supports the observed
426 | decrease of Si concentrations from July to November 2011. Brucite was therefore the main but not
427 | the only source of Mg in interstitial water of the experimental cells, which is consistent with kinetic
428 | tests completed in the laboratory (Kandji et al., 2017). During this transitional regime, the saturation
429 | indices of all carbonates increase, and several become over-saturated such as magnesite,
430 | nesquehonite aragonite and calcite (Figure 7).

431 | 5.1.2 Seasonal regime

432 | Since 2012, leachate water from cells EC-1 and EC-2 has been characterized by high
433 | concentrations of Mg, ranging from 50 to 180 mg/L, and a pH ranging from 8.1 to 10 in which
434 | HCO₃⁻ is the dominant carbonate species (Appelo and Postma 2005). The leachate water from both
435 | cells is therefore similar to a Mg-HCO₃⁻ - type, or type I water, characteristic of open-system
436 | interaction between CO₂-bearing meteoric water and ultramafic rocks (Bruni et al., 2002; Cipolli et
437 | al., 2004; Marques et al., 2008; O'Neil and Barnes, 1971; Oskierski et al., 2016; Paukert et al., 2012;
438 | Rollo and Jamieson, 2006). Nevertheless, dissolution of CO₂ in interstitial water is the first limiting
439 | step of carbon mineralization in the experimental cells; (Gras et al., 2017), and the leachate water
440 | geochemistry indicates that reactions occur in an open system with atmospheric CO₂. The pH,
441 | alkalinity, and the Si, Mg, Ca, K, and Na concentrations from leachate waters in both cells evolved
442 | seasonally while concentrations from other chemical components were stable or below detection
443 | (Figures 6 and 7) (Supplementary information). These seasonal variations of leachate geochemistry
444 | can be explained by: (1) changes in the hydrologic regime (Nordstrom, 2011, 2009), and (2)
445 | changes of the equilibrium conditions between the carbon mineralization reactions (Wilson et al.,
446 | 2010).

447 | Changes in hydrological regimes at mine waste sites over time can have important impacts
448 | on water quality (Nordstrom, 2011). During dry periods, for example, the concentration of
449 | dissolved metals increases slowly in the leachate water. In contrast, the first strong rainstorm
450 | following a dry period (first flush), or an intense rain event, may cause an abrupt increase of

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451 concentrations followed by a decrease (Nordstrom, 2011, 2009). The climate near Amos (Quebec),
452 is characterized by large changes in environmental conditions over the year (Table 1). During
453 winter, precipitation is lowest, and the water content in both cells is minimal, near the field capacity
454 and the permanent wilting point. Despite these conditions, carbon mineralization should be effective
455 and carbonates such as landsfordite, could precipitate (Beinlich and Austrheim, 2012; Ulven et al.,
456 2017; Zarandi et al., 2016). Spring snowmelt induces a first flush of water after the relative dry
457 winter period, which was observed in May 2016 as an increase in water content at all depths in cell
458 EC-2. Such a first flush in spring or intense rain events throughout the year may have impacted the
459 leachate water geochemistry and could explain abrupt changes. Each year, the Mg concentrations
460 and alkalinity values tend to be higher in the spring (May and June) and fall (September to
461 November), and lowest in the summer (July and August). These trends are inverse with that of
462 precipitations. It thus seems that Mg concentrations and alkalinity values (related to DIC) might be
463 controlled, at least in part, to dilution from rain and snowmelt water. However, no general co-
464 evolution between leachate geochemistry and snow melting or rain events has been observed.

465 Every year, between May and July, the temperature and solar radiation increased, while from
466 August to October a decrease was observed. The relative humidity in the atmosphere and total
467 precipitation were slightly lower from May to July than between August to October. Additionally,
468 during the summer, rain events were slightly less frequent (Figures 5 and 6) (Table 1). Decreasing
469 rainfall events between May and July caused a deficit of water in the cells, over a period during
470 which temperature and solar radiation were conducive to evaporation. During this period, a
471 decrease in water content at 4 cm depth in EC-2 was observed in 2013 and 2014. Similarly, between
472 the end of July and November of each year, increases in precipitation caused ingress of water within
473 the cells and in 2016, the water content at 4 cm depth increased in cell EC-2 (Figure 4 and Table 1).

474 Potassium and sodium ions react little during transport in the experimental cells and are
475 thus considered conservative in this study. Furthermore, these elements were not affected by
476 changes in equilibrium of the carbon mineralization reactions. During dry seasons (May to July),
477 when evaporation was highest, K, Na, Si and Ca concentrations increased. In contrast, when
478 precipitation then increased (August to November), concentrations of K, Na, Si, Ca, decreased.
479 Changes in the hydrological regimes over the year then impacted leachate water quality in the DNP
480 residues. However, the decrease of magnesium concentrations during this seasonal regime, is not
481 directly correlated with changes in precipitation and evaporation conditions, and is not yet fully
482 understood.

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483 Changes in evaporation conditions and in watering may alter the equilibrium between the
484 three principal reactions of carbon mineralization presented earlier: (3) dissolution of CO₂ in water,
485 (4) dissolution of reactive minerals, and (5) carbonate precipitation (Assima et al., 2012; Kandji et
486 al., 2017b; Wilson et al., 2014; Zarandi et al., 2017b). Dissolution of CO₂ in interstitial waters
487 contributes to the dissolved inorganic carbon which produces bicarbonate (HCO₃⁻) and carbonate
488 (CO₃²⁻) ions. Reaction 4 releases magnesium ions in the interstitial water, while reaction (5)
489 consumes magnesium ions and bicarbonate ions. Changes in climatic conditions and precipitation
490 could promote one of these three reactions over the others and induce disequilibrium which in turn
491 would modify the leachate water geochemistry (Beinlich and Austrheim, 2012; Wilson et al., 2010).

~~492 ——— Between May and July, maximum evaporation promoted carbonate mineral precipitation in
493 cells EC 1 and EC 2. Gras et al. (2017) documented the impacts of evaporation on isotopic
494 compositions of neo-formed carbonate minerals. This carbonate precipitation decreases magnesium
495 and dissolved inorganic carbon concentrations in leachate water. Increasing carbonate precipitation
496 over other carbon mineralization reactions, observed between May and July, might have led to the
497 observed decrease of magnesium concentrations in leachate waters from cells EC 1 and EC 2
498 (Figures 5 and 6). Additionally, from May to July, slightly reduced rainfall increased the leachate
499 water residence time in the experimental cells, thus the leachate would have remained longer in a
500 CO₂-poor environment where dissolution of CO₂ in pore water was limited (Gras et al., 2017,
501 Lechat et al., 2016; Oskierski et al., 2016). Bicarbonate ions consumed by carbonate mineral
502 precipitation could therefore not be replaced by dissolution of CO₂ from the atmosphere. The
503 decrease of DIC concentration in leachate waters from EC 1 and EC 2 is induced by consumption
504 of bicarbonate ions during carbonate precipitation. This is also consistent with the decrease of pCO₂
505 calculated using Phreeqc (Supplementary information). The main contributors to alkalinity in
506 leachate water from cells EC 1 and EC 2 were bicarbonate and carbonate (CO₃²⁻). Consumption of
507 bicarbonate ions and a decrease of alkalinity might, at least in part, have led to a decrease of pH
508 from May to July. Moreover, the increase of orthosilicic acid in the water related to the increase of
509 silica concentration, might had led to the annual drop in pH. During carbon mineralization in the
510 laboratory and in natural environments, decreases in magnesium concentration and DIC caused by
511 carbonate precipitation have been previously described (Bruni et al., 2002; Cipolli et al., 2004;
512 Harrison et al., 2013; Lechat, 2016; Paukert et al., 2012; Wilson et al., 2010). Similarly, when
513 precipitation increased from July until November, fresh water percolated through the residue, the
514 residence time of water decreased, and the meteorological conditions were less favourable for
515 evaporation. Decreasing carbonate precipitation and the return to equilibrium between the carbon~~

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516 ~~mineralization reactions then led to an increase of magnesium and DIC concentrations, and to~~
517 ~~increased alkalinity (Figures 5 and 6). Displacement of the equilibrium between the three carbon~~
518 ~~mineralization reactions, leading to an increase in carbonate precipitation, therefore contributed to~~
519 ~~the seasonal regimes in the experiment cell leachate waters.~~

520 From year to year, the intensity of the seasonal cycles in Mg concentrations and alkalinity
521 seems to decrease, particularly in cell EC-2, while the pH slightly increases (Figures 5 and 6). This
522 long-term evolution could be related to a decrease of carbonate precipitation over the years. Indeed,
523 Gras et al. (2017) demonstrated that, since 2012, the decrease in CO_{2(g)} consumption capacity of
524 cells EC-1 and EC-2 was associated with the decrease in brucite content near the surface and due to
525 surface passivation (Assima et al., 2012; Harrison et al., 2015; Zarandi et al., 2016). Near the
526 surface, a decrease of magnesium in the leachate waters, related to the smaller proportion of brucite,
527 may limit the precipitation of carbonates (which would otherwise be promoted by evaporation) and
528 might explain the long-term geochemical evolution (Figures 5 and 6). Furthermore, a decrease of
529 porosity near the surface, caused by carbonate precipitation, may also alter the carbon
530 mineralization reactions which would also impact the leachate water geochemistry from year to
531 year (Acero et al., 2007; Beinlich and Austrheim, 2012). Further investigations are needed to
532 confirm and understand the long-term evolution of leachate water geochemistry.

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533 In summary, results have shown that leachate water geochemistry from the experimental
534 cells EC-1 and EC-2 was influenced by (1) the local weather (temperature, relative humidity, and
535 precipitation) and (2) evolution of the equilibrium between the governing carbon mineralization
536 reactions, leading to an increase of carbonate precipitation.

537 **5.2 Carbonate precipitation**

538 The evolution of leachate geochemistry presented in the previous section influences the
539 carbonate precipitation reactions. Thermodynamic equilibrium calculations reveal that, despite the
540 differences between cells EC-1 and EC-2, the saturation indices of the carbonate minerals have
541 been similar since 2011. However, the saturation indices evolve following seasonal changes of pH,
542 alkalinity and Mg concentrations (Figure 7). The saturation indices of all carbonate minerals first
543 decreased between May and July, then increased until November. Despite these variations, calcite,
544 aragonite and magnesite were over-saturated, since 2011, in leachate water from both cells.
545 Notwithstanding the oversaturation, Ca concentrations were not affected by the increase of
546 carbonate precipitation between May and July. The leachate waters from EC-1 and EC-2 were

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547 characterized by high Mg concentrations which can inhibit calcium carbonate precipitation
548 (Hopkinson et al., 2008). Inhibition of calcium carbonate precipitation can explain why Ca
549 concentrations did not change over seasonal cycles and is further consistent with the low modal
550 proportion of neo-formed calcium carbonates observed in this study and by Gras et al., (2017).
551 Saturation indices of artinite and hydromagnesite reflected either over- or under-saturated
552 conditions, whereas nesquehonite was under-saturated (Figure 7). It is important to note that
553 evaporation of leachate water, which may significantly increase the carbonate saturation indices,
554 was not considered here. Oskierski et al. (2016), for example, demonstrated that evaporation of 20%
555 of the leachate water from the Woodsreef mine induced oversaturation for hydromagnesite. At the
556 surface of the cells, where evaporation was highest, the carbonate minerals were therefore most
557 likely over-saturated. Nevertheless, changes in leachate water geochemistry, between May and
558 July, decreased the carbonate mineral saturation indices and thus these carbonate minerals became
559 under-saturated deeper within the cells. The increase in carbonate precipitation between May and
560 July, which altered the leachate water geochemistry, therefore created a feed-back loop limiting the
561 carbon sequestration potential of the cells.

562 In experimental cells EC-1 and EC-2, the neo-formed carbonate minerals trap atmospheric
563 CO₂ (Gras et al., 2017). In surface samples from both cells, artinite, nesquehonite, dypingite, and
564 hydromagnesite were observed, with rare aragonite. The amount of bound carbon depends on the
565 specific mineral. Nesquehonite has a ratio of CO₂ to Mg of 1, whereas the ratio is 4/5 for
566 hydromagnesite and dypingite. The stability of magnesium carbonate minerals increases from
567 lansfordite and artinite to nesquehonite, then dypingite, hydromagnesite, and stable magnesite,
568 ~~through to higher stability minerals of nesquesonihte, dypingite and hydromagnesite~~ (Canterford et
569 al., 1984; Hopkinson et al., 2008; Langmuir, 1965). At temperatures above 25°C, hydrous-
570 carbonates can evolve from lansfordite to nesquehonite (Beinlich and Austrheim, 2012; Hopkinson
571 et al., 2008), whereas nesquehonite can be converted to dypingite and hydromagnesite during
572 associated wetting/drying cycles and increasing temperature (Hopkinson et al., 2008; Oskierski et
573 al., 2016; Power et al., 2009; Wilson et al., 2009; Zarandi et al., 2017b). Hydromagnesite was more
574 common in samples from EC-1, whereas in EC-2 the main carbonate was dypingite. In cell EC-1,
575 the blocks of waste rock which were more conducive to wetting/drying cycles and evaporation,
576 were coated with carbonate minerals. Conversion from the less stable phases (artinite,
577 nesquehonite) to hydromagnesite was favoured in cell EC-1 which can explain the higher
578 proportion of hydromagnesite in EC-1. In contrast, the finer grain size of the tailings in cell EC-2
579 maintains a higher water content (Figure 4), which may slow the rate of dehydration of

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580 nesquehonorite to hydromagnesite. ~~Microorganisms-Fungi~~ at the surface of cell EC-2 (Figures 8 h)
581 could also promote precipitation of dypingite (McCutcheon et al., 2016; Power et al., 2010, 2009).
582 The grain size of the mining residue may therefore influence the type of carbonate minerals
583 precipitated, whereas evaporation and wetting-drying cycles control the conversion. Clearly, the
584 hydrogeological conditions can therefore also influence the quantity of carbon trapped in the
585 residues. In deeper EC-2 samples, however, only hydrotalcite supergroup minerals formed
586 (Supplementary information). As described in previous studies, in both cells EC-1 and EC-2, for
587 example, hydrotalcite supergroup minerals had formed during atmospheric weathering (Gras et al.,
588 2017; Oskierski et al., 2016; Turvey, 2015; Turvey et al., 2017). These minerals precipitated rapidly
589 after exposure to the atmosphere through weathering of brucite under CO₂ - limited conditions
590 (McCutcheon et al., 2016; Mumpton and Thompson, 1966; Turvey et al., 2017).

591 In cell EC-1, carbonate coatings may also have contributed to surface passivation (Figures 2
592 c, d and 8 a,b) (Assima et al., 2012; Zarandi et al., 2017b), whereas in cell EC-2, the carbonates
593 cemented the tailing grains, causing a decrease in porosity and permeability (Acero et al., 2007)
594 (Figures 2 h and 8 e). Therefore, precipitation of carbonates within the cells may decrease
595 atmospheric CO₂ consumption. In order to characterize the carbonate matrix interface, EPMA
596 analysis was used on waste rock samples from EC-1. In order to identify the minerals at the
597 carbonate-matrix interface, chemical analyses and theoretical mineral compositions have been
598 plotted on ternary diagrams (Figure 9). Most often, the carbonate-matrix interface is sharp, and the
599 chemical composition changed from serpentine to carbonates or brucite (Figure 9 c). However, on
600 several samples the chemical compositions of minerals at the carbonate-matrix interface range from
601 the pole of serpentine to a magnesium pole depleted in silica which corresponds either to brucite or
602 carbonates (Figure 9 a,b). Because the EPMA beam size (10 μm) is in some places larger than the
603 target minerals, superposition of serpentine or epoxy and carbonates may have altered the signal to
604 the measured composition. Nevertheless, the range of composition from the pole of serpentine to
605 the magnesian pole is consistent with the incongruent dissolution of serpentine in high pH water, in
606 which Si will be preferentially released over Mg (Pokrovsky and Schott, 2000; Ruiz-Agudo et al.,
607 2012).

608 The EPMA analyses did not allow precisely identifying the carbonate minerals in the mining
609 residues. In addition, the BSE images revealed that carbonate minerals at the surface were fragile
610 (Figure 9 a) and filled the fractures at the expense of brucite (Figures 9 b and c). Frost cycles and
611 dehydration of the carbonate minerals increased the fracturing of waste rock ~~bloeks-fragments~~ and
612 thus the carbonate coating may have been peeled off (Beinlich and Austrheim, 2012; Ulven et al.,

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613 | 2017; Zarandi et al., 2017b, 2016). Carbonate precipitation therefore contributes to (1) exposure of
614 | fresh serpentine to weathering, which maintains atmospheric CO₂ sequestration, and (2) increased
615 | surface passivation, which may decrease atmospheric CO₂ consumption. Carbonate precipitation
616 | dynamics in the DNP residues, which changed leachate water geochemistry, thus decreased porosity
617 | and permeability, promoted fracturation of the mining residues and caused surface passivation,
618 | creating a feed-back loop limiting the carbon sequestration potential.

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619 | 5.3 Quantification of atmospheric CO₂ sequestration

620 | Carbon sampling of cell EC-1 was limited to surface samples, and therefore it was not
621 | possible to accurately quantify the carbon sequestered. However, extensive sampling at the center
622 | and at the edges of cell EC-2 allowed tracking the evolution of carbon sequestration over time and
623 | thus allowed estimating the quantity of captured CO₂.

624 | At the center of cell EC-2, the inorganic carbon content increased slowly from year to year
625 | (Gras et al., 2017) but changed seasonally. Most notably, the carbon content was higher in summer
626 | than in autumn or spring (Figure 10). Dissolution of less stable neo-formed carbonate minerals
627 | during rain events (Ulven et al., 2017) or changes in water geochemistry (Figures 5 and 6) may
628 | have led to these seasonal variations of the carbon content. However, the cores were randomly
629 | sampled at the center of the cell, irrespective of surface mineralization, and carbon mineralization at
630 | the surface of the cell was not continuous or homogeneous as shown by an evaporitic crust and
631 | cones (Figures 2, and 11). In addition, the carbonate crusts were thin and fragile and might have
632 | been disturbed over time (Figure 2 h). The small seasonal variations might therefore be an artifact
633 | induced by the sampling process. Additional analyses are necessary to better understand the annual
634 | evolution of the carbon content in experimental cell EC-2.

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635 | The inorganic carbon content in cell EC-2 also varied laterally. At the center of the cell, for
636 | example, the carbon content was lower and the carbonation front shallower than at the edges of the
637 | cell (Figure 11). The water content, at the center of cell EC-2 was near 25 % at 4 cm depth since
638 | 2011, but below this depth the water saturation reaches 25 to 40 % (Figure 4). Since the mean
639 | porosity of the tailings in cell EC-2 was 44%, the residues were therefore almost fully saturated
640 | below 4 cm depth. Towards the edges the residue thickness decreases, and the impact of
641 | evaporation became gradually more important such that mean water content became lower.
642 | Previous studies have shown that high and low water saturations tend to reduce the carbon
643 | mineralization reaction rates (Assima et al., 2013, 2012; Awoh et al., 2014; Harrison et al., 2015).

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644 In cell EC-2, the watering frequency corresponds to actual rainfall events and thus was the same at
645 the center and the edges of the cell. Carbon mineralization was thus more efficient near the edges of
646 the cell because of the lower water saturation compared to the center of the cell. Similarly, under
647 the wood plank (Figure 2 g), the residues are partially protected from ~~precipitation-rain fall~~ and the
648 water content was lower, thus carbon mineralization was likely more efficient yielding a higher
649 carbon content (Figures 2 e and 11). In contrast, the capture of carbon near the center of cell EC-2
650 was inhibited by the higher water content in the mining residues. Alternatively, sheltering from rain
651 by the wood plank may have prevented carbonate dissolution, as argued by Ulven et al. (2017)

652 The quantity of CO₂ sequestered within the experimental cell EC-2 was estimated using the
653 measured inorganic carbon content. The carbon of the core samples was weighted by the mass of a
654 layer using the thickness of the core sample. For the three upper layers, two-thirds of the volume
655 was ascribed to the central core, and one-third to the core from the edge of the cell (Figure 11).
656 With this approach, ~~in-up to~~ May 2015, an estimated 13 kg of atmospheric CO₂ was sequestered by
657 the mining residues in cell EC-2, which corresponds to a mean rate of 1.4 (+/-
658 0.3) kgCO₂/tonne/year. This rate is about twice as high as the rate calculated by Bea et al., (2012)
659 using numerical simulations for tailing pounds near Mount Keith (Australia). The DNP residues,
660 however, are characterized by a higher brucite content (10.2 vol%) (Assima et al., 2012) compared
661 to the tailings of the Mount Keith mine (2.5 vol%). Brucite is a key mineral which reacts quickly
662 during carbon mineralization and controls its extent (Assima et al., 2013; Pronost et al., 2012;
663 Harrison 2013, 2015, 2016, 2017; Kandji et al., 2015). It is therefore likely the higher brucite
664 content in the DNP residues may have induced the higher sequestration rate. The DNP mine will
665 generate, each year, approximately 15 Mt of tailings and release about 127,700 tonnes of CO₂
666 (Staples et al., 2013; Kandji et al., 2017b). Using the sequestration rate of the experimental cell EC-
667 2, the tailing residues will sequester about 21 kt of atmospheric CO₂ each year, which represents
668 around ~~one-quarter~~ 16% of the CO₂ emitted. This rate of sequestration is lower than the rate
669 calculated from laboratory kinetic tests (8.5 kgCO₂/tonne) (Kandji et al., 2017). The contrast
670 between laboratory and natural conditions may be explained by differences in
671 precipitation/watering and climatic conditions (Temperature, RH). Additionally, the experimental
672 cell EC-2 was frequently flooded after intense rain events and during the summer's drought cracks
673 were observed. These extreme water contents limited the carbonation of the residues and may
674 explain the difference between the laboratory and experimental cell tests. In cell EC-1, the
675 hydrogeological properties, which control the fluid flow and influence the mineral carbonation, are
676 different than in EC-2. In addition, the hydrogeological properties are very heterogeneous (Aubertin

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677 et al., 1996). Therefore, the results from EC-2 cannot be easily extrapolated, and the estimated
678 amounts of CO₂ capture might be quite different from the real amounts sequestered (Awoh et al.,
679 2014; Lechat et al., 2016).

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680 **6. CONCLUSION**

681 Two experimental cells were used to study impacts of atmospheric weathering on passive
682 carbon mineralization in mining residues from the Dumont Nickel Project. The mining residues
683 filling the experimental cells had a similar mineralogy and were submitted to the same weather
684 conditions (temperature, RH, precipitation). However, the hydrogeological properties, which
685 influence the supply of CO₂ and the water content of the cells, were different. Despite these
686 hydrogeological differences, the same processes control the evolution of leachate water
687 geochemistry. High magnesium concentrations and a moderate to alkaline pH characterize the
688 leachate water from both cells, which is consistent with weathering of ultramafic rocks in a system
689 open to CO₂. Seasonal variations of leachate water geochemistry are caused by (1) seasonal and
690 longer-term changes in rainfall and weather conditions, and (2) a displacement of the equilibrium
691 between the carbon mineralization reactions. Between May and July each year, leachate water flows
692 in a CO₂- depleted environment where supply of atmospheric CO₂ to water is limited (Gras et al.,
693 2017). During this period, evaporation is at its maximum, therefore precipitation of carbonate
694 minerals increases causing a decrease in magnesium concentration and alkalinity. Seasonal
695 variations in leachate water geochemistry also impact the saturation indices of carbonate minerals.
696 Between May and July, hydromagnesite and artinite become under-saturated which limits carbon
697 sequestration. Furthermore, carbonate precipitation, self-limits carbon sequestration through a
698 negative feed-back loop.

699 Over the years, magnesium concentrations and alkalinity decrease which is related to a
700 decrease of CO₂ consumption (Gras et al., 2017). In experimental cells EC-1 and EC-2, carbonate
701 precipitation is mainly driven by evaporation. Dehydration of nesquehonite to hydromagnesite is
702 promoted by the larger grain size in EC-1 and dypingite is more common in EC-2. Since the
703 hydrogeological properties of EC-2 are similar to a silty-clay porous medium, a high liquid/solid
704 ratio is maintained, and residues are nearly saturated at shallow depths which limits carbonate
705 precipitation. Approximately 13 kg (+/- 1) of atmospheric CO₂ were sequestered in cell EC-2
706 between 2011 and 2015, which corresponds to a mean rate of 1.4 (+/-0.3) kgCO₂/tonne/year.
707 However, the carbon sequestration capacity was inhibited by the high water content.

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9 708 This study underlines the critical impact of hydrogeological properties and leachate water
10 709 geochemistry on atmospheric CO₂ sequestration capacity of ultramafic mine wastes. Changes in
11 710 these properties during passive carbon mineralization must be addressed in order to optimise
12 711 atmospheric CO₂ sequestration in large-scale mining waste deposits.

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15 712 **Acknowledgements**

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19 714 **Figure 1 :** a) Site location and b) geological context of the proposed DNP mine site and Dumont sill.

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21 715 **Figure 2 :** Textures in the experimental cells EC 1 and EC 2. a) General view of waste rock cell EC 1 with
22 716 pluri-centimetric blocks at the surface, b) white crusts coating surfaces and fractures in samples from EC 1, c)
23 717 surface of a pluri-centimetric block in EC 1 coated with white crusts, d) white crust observed with binocular
24 718 magnifier, with several phases of precipitation visible, e) general view of the tailings cell EC 2, f) evaporitic
25 719 structure (cones) observed at the edges of cell EC 2, g) residues cemented and covered with white crust below
26 720 the wood support beam at the edges of cell EC 2, h) indurated flat crust, sampled at the edge of cell EC 2.

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28 721 **Figure 3 :** Evolution of water flux at the bottom of the experimental cells in 2013.

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30 722 **Figure 4 :** Water content evolution with depth in EC 2 and rainfall in 2016.

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32 723 **Figure 5 :** Evolution of chemical composition of leachate in EC 1 since 2011.

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34 724 **Figure 6 :** Evolution of chemical composition of leachate from EC 2 since 2011.

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36 725 **Figure 7 :** Evolution of saturation indices of the main carbonate minerals.

37 726 **Figure 8 :** Scanning electron micrographs of surface samples from EC 1 and EC 2. a) Surface of a white
38 727 crust sampled in cell EC 1; depressions are filled with fissured carbonates whereas on the top well-crystallized
39 728 carbonates are visible, b) serpentine grain, from cell EC 1, partially covered with flaky carbonate minerals, c)
40 729 white crust, from cell EC 1, with well-crystallized hydromagnesite, d) needle of well-crystallized aragonite
41 730 observed on sample surface from EC 1, e) surface of a flat crust, from EC 2. Carbonate minerals have coated
42 731 the surface and cemented the tailings grains, f) Serpentine grain, from flat crust in EC 2, partially covered
43 732 with flaky carbonates overcome by well-crystallized nesquehonite, g) different sizes of nesquehonite crystals
44 733 observed on a surface sample from EC 2, h) intergrowth of microbial mats and carbonate minerals observed
45 734 at the surface of cell EC 2.

46 735 **Figure 9 :** Back-scattered electron micrographs of polished thin sections from cell EC 1 and EPMA chemical
47 736 compositions reported on ternary diagrams.

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49 737 **Figure 10 :** Inorganic* carbon content at the center of cell EC 2

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51 738 **Figure 11 :** Cross-section of cell EC 2 in May 2015 and contoured inorganic carbon content. We thank RN
52 739 an anonymous reviewer for their comments which helped improve the paper significantly.

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Figure captions

Figure 1 : a) Site location and b) geological context of the proposed DNP mine site and Dumont sill.

Figure 2 : Textures in the experimental cells EC-1 and EC-2. a) General view of waste-rock cell EC-1 with pluri-centimetric blocks at the surface, b) white crusts coating surfaces and fractures in samples from EC-1, c) surface of a pluri-centimetric block in EC-1 coated with white crusts, d) white crust observed with binocular magnifier, with several phases of precipitation visible, e) general view of the tailings cell EC-2, f) evaporitic structure (cones) observed at the edges of cell EC-2, g) residues cemented and covered with white crust below the wood support beam at the edges of cell EC-2, h) indurated flat crust, sampled at the edge of cell EC-2.

Figure 3 : Evolution of water flux at the bottom of the experimental cells in 2013.

Figure 4 : Water content evolution with depth in EC-2 and rainfall in 2016.

Figure 5 : Evolution of chemical composition of leachate in EC-1 since 2011.

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1026 **Figure 6 : Evolution of chemical composition of leachate from EC-2 since 2011.**

1027 **Figure 7 : Evolution of saturation indices of the main carbonate minerals.**

1028 **Figure 8 : Scanning electron micrographs of surface samples from EC-1 and EC-2. a)**
1029 **Surface of a white crust sampled in cell EC-1; depressions are filled with fissured**
1030 **carbonates whereas on the top well-crystalized carbonates are visible, b) serpentine grain,**
1031 **from cell EC-1, partially covered with flaky carbonate minerals, c) white crust, from cell**
1032 **EC-1, with well-crystalized hydromagnesite, d) needle of well-crystalized aragonite**
1033 **observed on sample surface from EC-1, e) surface of a flat crust, from EC-2. Carbonate**
1034 **minerals have coated the surface and cemented the tailings grains. f) Serpentine grain, from**
1035 **flat crust in EC-2, partially covered with flaky carbonates overcome by well-crystalized**
1036 **nesquehonite, g) different sizes of nesquehonite crystals observed on a surface sample from**
1037 **EC-2, h) intergrowth of fungi and carbonate minerals observed at the surface of cell EC-2.**

1038 **Figure 9 : Back-scattered electron micrographs of polished thin sections from cell EC-1**
1039 **and EPMA chemical compositions reported on ternary diagrams.**

1040 **Figure 10 : Inorganic* carbon content at the center of cell EC-2**

1041 **Figure 11 : Cross-section of cell EC-2 in May 2015 and contoured inorganic carbon**
1042 **content,**

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5 1 **Atmospheric carbon sequestration in ultramafic mining residues**
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7 2 **and impacts on leachate water chemistry at the Dumont Nickel**
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16 5 A. Gras^{1*}, G. Beaudoin¹, J. Molson¹, B. Plante²,
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27 9 **Abstract**
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30 10 Passive carbon mineralization in ultramafic mining residues, which allows the sequestration
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32 11 of CO₂ through carbonate precipitation, is one of the options being considered to limit the
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34 12 accumulation of anthropogenic CO₂ in the atmosphere. The Dumont Nickel Project (DNP) will
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36 13 generate approximately 1.7 Gt of ultramafic mining residues over 33 years of production and the
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38 14 mine will release about 127,700 tonnes of CO₂ each year. Using two experimental cells filled with
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40 15 ultramafic waste rock (EC-1) and milling residues (EC-2), the impacts of carbon mineralization on
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42 16 leachate water quality were studied and the quantity of sequestered carbon was estimated.
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44 17 Hydrotalcite supergroup minerals, aragonite, artinite, nesquehonite, dypingite and hydromagnesite
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46 18 precipitated through atmospheric weathering, while the inorganic carbon content of the weathered
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48 19 mining waste increased from 0.1 wt% to 4.0 wt% which indicate active CO₂ sequestration. The
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50 20 leachate water, sampled at the bottom of the experimental cells, is characterized by an alkaline pH
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52 21 (~9.5), a high alkalinity (~90 to ~750 mg/L) and a high concentration of magnesium (~50 - ~750
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54 22 mg/L), which is typical from weathering of ultramafic rocks in a system open to CO₂.

55 23 Since 2012, the chemical composition of the leachate water has evolved seasonally. These
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57 24 seasonal variations are best explained by: (1) climatic variations over the year and, (2) increased
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59 25 carbonate precipitation between May and July. Increased carbonate precipitation decreased the
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61 26 alkalinity and magnesium concentrations in the leachate water and produced pore waters which
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63 27 were undersaturated with respect to carbonate minerals such as artinite and hydromagnesite.
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4 28 Carbonate precipitation thus self-limits carbon sequestration through a negative feed-back loop. The
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6 29 carbon sequestration potential of the DNP residues is also influenced by the hydrogeological
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8 30 properties of the residues. In cell EC-2, a high liquid/solid ratio, which limits carbonate
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10 31 precipitation, was maintained by the hydrogeological properties. Since 2011, an estimate of 13 kg
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12 32 of atmospheric CO₂ has been sequestered in the milling residues (EC-2), which corresponds to a
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14 33 mean rate of 1.4 (+/- 0.3) kgCO₂/tonne/year. Using this mean rate, the 15 Mt of tailings produced
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16 34 each year, during the planned 33 years of mining operation, could potentially sequester 21,000
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18 35 tonne of CO₂ per year by passive carbon mineralization, about 16% of the 127,700 tonnes of CO₂
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20 36 annually emitted by the planned mining operation.

21 37 **1. Introduction**

23 38 Anthropogenic CO₂ released into the atmosphere is considered a major driver of global
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25 39 climate change (IPCC, 2014). In order to limit accumulation of gaseous CO₂ in the atmosphere,
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27 40 several methods of carbon sequestration are envisaged including carbon mineralization (IPCC,
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29 41 2005). As reviewed by Seifritz (1990), carbon mineralization technologies are derived from natural
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31 42 exothermic reactions, which occur spontaneously and trap CO₂ through carbonate precipitation
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33 43 (Berner and Kothavala, 2001; Gaillardet et al., 1999; Lackner et al., 1995). The general carbon
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35 44 mineralization reaction for silicate minerals such as serpentine is summarized in Reaction (1):



39 46 Carbon mineralization is attractive because no post-storage monitoring is necessary and carbon
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41 47 dioxide is sequestered over geological time scales. Two types of carbon mineralization are
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43 48 considered (Beaudoin et al., 2008; Gerdemann et al., 2007; Kelemen and Matter (2008); Matter et
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45 49 al. (2009); Olajire, 2013; Park and Fan, 2004; Pronost et al., 2011; Sanna et al., 2014; Sipilä et al.,
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47 50 2008; Teir et al., 2009) :

- 49 51 (1) in-situ carbonation, wherein pure CO₂ is injected into subsurface mafic
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51 52 formations to form carbonate minerals, and
- 52 53 (2) ex-situ carbon mineralization, which uses mining or industrial residues as the
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54 54 carbon sink.

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56 55 Natural weathering of ultramafic mining residues captures atmospheric CO₂ through
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58 56 passive carbon mineralization. Carbonation rates of up to 1700 g C m⁻² y⁻¹, for example, have been
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60 57 reported from historical and active mining sites. The main carbonate minerals precipitated in mining

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4 58 residues are pyroaurite-3R [$\text{Mg}_6\text{Fe}_2^{3+}(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$], nesquehonite [$\text{MgCO}_3\cdot 3\text{H}_2\text{O}$],
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6 59 dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 5\text{H}_2\text{O}$], hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 4(\text{H}_2\text{O})$], and aragonite
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8 60 [CaCO_3] (Beaudoin et al., 2008; Gras et al., 2017; Lechat et al., 2016; Oskierski et al., 2013; Power
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10 61 et al., 2013a, 2013b; Pronost et al., 2012; Rollo and Jamieson, 2006; Turvey et al., 2017; Wilson et
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12 62 al., 2011, 2006, 2014). Passive carbon mineralization has previously been studied by considering
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14 63 mineralogical evolution and leachate water geochemistry (Assima et al., 2014a, 2013; Beinlich and
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16 64 Austrheim, 2012; Harrison et al., 2017, 2013; Power et al., 2009; Rollo and Jamieson, 2006;
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18 65 Zarandi et al., 2017a, 2017b, 2016), and by analysing the stable carbon isotope (C^{13} and C^{12}
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20 66 composition of dissolved inorganic carbon (DIC) and neo-formed carbonates (Beaudoin et al.,
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22 67 2017, 2008; Gras et al., 2017; Harrison et al., 2016, 2013, Oskierski et al., 2013b, 2016, Wilson et
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24 68 al., 2014, 2011, 2009). Ex-situ, passive carbon mineralization in mining residues has two main
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26 69 advantages: (1) the mine wastes can be re-used for environmental benefit, and (2) CO_2 can be
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28 70 directly sequestered from the atmosphere. Moreover, these processes can potentially lead to
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30 71 developing carbon-neutral mines (Harrison et al., 2013; Hitch and Dipple, 2012; Mills et al., 2010;
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32 72 Power et al., 2014). The main disadvantage is the slow rate of reaction, compared to ex-situ carbon
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34 73 mineralization.

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36 74 The Dumont Nickel Project (DNP) of RNC Minerals (RNCM) is designed to produce 0.51
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38 75 Gt of ultramafic waste rock and 1.18 Gt of milling (tailings) residues (Staples et al., 2013). The
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40 76 carbon sequestration capacity of these future residues at high partial pressure of CO_2 , and the effect
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42 77 of mineralogy, water saturation, watering frequency, and temperature, have been well studied at the
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44 78 laboratory scale (Assima et al., 2014a, 2014b, 2013, 2012, Kandji et al., 2017b, 2015; Plante et al.,
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46 79 2014; Pronost et al., 2010; Zarandi et al., 2016, 2017a, 2017b). However, in order to develop useful
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48 80 engineered solutions for carbon sequestration, and to properly estimate the carbon sequestration
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50 81 capacity, more realistic field experiments are required (Olajire, 2013; Lechat et al., 2016; Gras et
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52 82 al., 2017).

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54 83 Using two experimental cells, Gras et al. (2017) demonstrated that between the three
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56 84 potential sources of CO_2 , notably: (1) the atmosphere, (2) organic matter oxidation and (3)
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58 85 carbonate dissolution, atmospheric CO_2 was the main source of sequestered carbon during natural
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60 86 atmospheric weathering of the DNP residues. In addition, Gras et al. (2017) showed that dissolution
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62 87 of atmospheric CO_2 in interstitial water was the first step which limited the carbon mineralization
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64 88 capacity. However, additional factors can also limit the mineralization capacity. For example,
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66 89 natural weathering of ultramafic rocks will change the geochemistry of meteoric water which
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68 90 percolates through the mining residues (Rollo and Jamieson 2006; Beinlich et al., 2012; Oskierski et

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4 91 al., 2016) and natural terrain (Bruni et al., 2002; Cipolli et al., 2004; Marques et al., 2008; Paukert
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6 92 et al., 2012). Since changes in the water chemistry can affect carbonate precipitation, they may
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8 93 therefore also impact the carbon sequestration potential of mine residues (Appelo and Postma,
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10 94 2005).

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12 95 In this contribution, using two field experimental cells, EC-1 filled with mine waste, and
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14 96 EC-2 which contains milling residue from the DNP, we report on changes in (1) leachate water
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16 97 geochemistry, (2) waste mineralogy, and (3) carbon content. In addition, the effects of
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18 98 hydrogeological properties and leachate water geochemistry on carbonate mineral precipitation are
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20 99 investigated. Finally, the amount of atmospheric CO₂ trapped during atmospheric weathering of the
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22 100 DNP residues is estimated.

23 101 **2. Geological setting**

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26 102 The DNP site is located near the town of Amos in north-western Québec (Figure 1a). The
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28 103 deposit is hosted in a sill which had intruded into rock of the Superior province of the Canadian
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30 104 Shield. Two distinct units are identified in the sill: (1) a mafic zone of gabbro which is overlain by
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32 105 (2) an ultramafic zone formed by peridotite and dunite (Figure 1b) (Duke, 1986; Eckstrand, 1975;
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34 106 Sciortino et al., 2015). The ultramafic zone, which contains a resource of 1.72 Mt of nickel ore, is
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36 107 approximately 6.8 km long with an average thickness of 450 m. In the Dumont sill, nickel
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38 108 enrichment of intercumulus minerals is a product of serpentinization (Duke, 1986; Sciortino et al.,
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40 109 2015) which is a hydrothermal process involving water and heat which alters silicate minerals, such
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42 110 as olivine [(Mg,Fe,Ni)₂SiO₄], to serpentine minerals [(Mg,Fe,Ni)₃Si₂O₅(OH)₄], as well as to brucite
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44 111 [Mg(OH)₂] and magnetite [Fe²⁺Fe³⁺O₄]. The dunite protolith was composed of Ni-rich olivine with
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46 112 horizons rich in sulfide minerals. During serpentinization, the nickel was redistributed in
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48 113 intercumulus pentlandite [(Fe,Ni)₉S₈], awaruite [Ni₃Fe] and heazlewoodite [Ni₃S₂] (Sciortino et al.,
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50 114 2015). The main mineral assemblage in the dunite subzone consists of lizardite, magnetite, brucite,
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52 115 and chlorite, with variable amounts of pentlandite, awaruite, and heazlewoodite (Sciortino et al.,
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54 116 2015; Staples et al., 2013). The DNP is expected to generate approximately 1.7 Gt of ultramafic
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56 117 mining residue of two types: (1) ~1.18 Gt of tailing residues issued from the metallurgical
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58 118 processes, and (2) ~510 Mt of waste rocks (Staples et al., 2013).

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119 **3. Materials and Methods**

120 **3.1 Experimental cells:**

121 Near the planned DNP mining site near Amos, Quebec, two experimental cells were built
122 and instrumented in order to study weathering of the mine’s ultramafic mining residues. Gras et al.
123 (2017) provide detailed descriptions of the experimental cells. The first cell (EC-1) was filled using
124 104 tonnes of waste rock from blasting of a dunite outcrop (Figure 1b). The grain size of waste rock
125 in EC-1 ranged from milimetric to pluricentrimetric blocs. The second cell (EC-2) contains
126 approximately 2.6 tonnes of milling residues containing the slimes, fluff and rougher tails (non-
127 magnetic) produced in a pilot plant. The run of mine ore, processed in the pilot plant, was taken
128 from four boreholes located in the dunite subzone (Figure 1b) (Staples et al., 2013). The pilot-plant
129 process consisted of two cycles of grinding, desliming, and flotation in a hydrocyclone followed by
130 magnetic separation. During the first cycle, the run of mine ore was crushed and ground in wet
131 media with the dispersant Calgon © (500 g/t) and potassium amyl xanthate (PAX) (150 g/t) to 80%
132 passing minus 150 µm, then the non-magnetic portion from the first cycle was crushed and ground
133 in wet media to 80% passing minus 74 µm for the second cycle of deshalming and flotation.

134 Within both experimental cells, gas sampling ports were installed in order to monitor CO₂
135 concentrations within the interstitial air (Gras et al., 2017). In addition, cell EC-2 contained a
136 Decagon 5TM probe, 4 cm below the tailings surface, to monitor changes in volumetric water
137 content and temperature. In November 2015, two additional Decagon 5TM probes were placed at
138 14 and 25 cm depths to measure changes in water content and temperature with depth. At the
139 bottom of cells EC-1 and EC-2, a geomembrane and a drain were installed to collect the leachate
140 water. Both drains were connected to tipping bucket rain gauges to log the flux of water at the
141 output of the cells. A weather station recorded solar radiation, temperature, wind speed and
142 direction, and a tipping bucket rain gauge measured rainfall.

143 **3.2 Leachate water analyses:**

144 Leachate water is produced from infiltration of rain and meltwater through the mining
145 residues in experimental cells EC-1 and EC-2. The leachate was sampled twice a month between
146 July 2011 and November 2013, and then monthly from May 2014 to November 2015. The leachate
147 water pH was measured on site, while samples were collected in bottles which were sent to
148 Maxxam Analytical (QC, Canada) and to SGS Canada (ON, Canada) to measure major and minor
149 ions and metals (Al, Sb, As, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cu, Sn, Fe, Li, Mg, Mn, Mo, Hg, Ni, Pb,

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150 K, Se, Si soluble in HNO₃, SO₄, Na, Sr, Tl, Ti, U, V, Zn), and total alkalinity, until 2015. The
151 geochemical model PhreeqC (Parkhurst et al., 1999) was used to calculate the saturation indices of
152 major carbonate minerals in the leachate water. Since the temperature of the leachate was not
153 measured, a temperature of 25°C was therefore used and after the method of Oskierski et al. (2016)
154 the thermodynamic equilibrium calculations were carried out using the Wateq4f database (Ball and
155 Nordstrom, 1991).

156 **3.3 White crusts and core samples:**

157 Within months of constructing the waste rock cell (EC-1), white crusts of a mineral
158 precipitate started to coat the surface of the rock fragments during atmospheric weathering. The
159 residues were sampled manually (Figure 2 a, b, c, d). White crusts of a mineral precipitate also
160 indurated the tailings surface near the edges of cell EC-2 which were also sampled (Figure 2 e, f, g,
161 h). Between 2012 and 2015, surface crusts were sampled 19 and 16 times in both EC-1 and EC-2,
162 respectively. In order to document the weathering processes acting on the residues, 7 cores, ranging
163 in length from 14 cm to 32 cm, were sampled from October 2013 to November 2015 in the center of
164 EC-2 using a steel tube (Gras et al., 2017). Additionally, two cores, 5 cm and 3 cm in length, were
165 sampled in October 2014 and May 2015. One core was sampled below a wooden access plank at the
166 edges of the cells and the other at the edges of the cell EC-2 (Figures 2 e and f) (Supplementary
167 information).

168 **3.4 Mineralogical analysis**

169 Crushed samples from cells EC-1 and EC-2 were analysed by XRD using a Siemens D5000
170 X-ray diffractometer (Cu-K α radiation). XRD patterns were collected with a scanning step of
171 1°/min (0.02° step size) over a 5-40° scattering angle range. The Jade computer program was used
172 to identify the mineral phases.

173 A JEOL 840-A scanning electron microscope (SEM) at Université Laval, Québec, equipped
174 with an Avalon (PGT) energy-dispersive X-ray spectrometer (EDS), was used in order to describe
175 mineral habits and texture, and for mineral identification of the neo-formed phases.

176 Polished thin sections of white crusts from EC-1 and EC-2 were analyzed using a
177 CAMECA SX-100 Electron Probe Micro-Analyzer (EPMA) at Université Laval. The device is
178 equipped with 5 wavelength-dispersive spectrometers. Chemical analyses were performed using a
179 15 kV accelerating voltage with a 20 nA beam current, and a 10 μ m beam size. Simple oxides

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180 (GEO Standard Block of P and H Developments) and/or natural minerals (Mineral Standard Mount
181 MINM 2553, Astimex Scientific; Jarosewich et al., 1980) were used to calibrate the instrument for
182 chemical analyses.

183 **3.5 Carbon content**

184 The total carbon content was measured with an Eltra CS 800 carbon and sulphur analyser at
185 Université Laval (Gras et al., 2017). High and low carbon contents were calibrated using,
186 respectively, AR 4018 (1.30 +/- 0.05 wt% C), and UB-N serpentine ANRT (0.106 +/- 0.08 wt% C).
187 The standards (Ar 4018 and UB-N serpentine) were analysed after every set of three analyses to test
188 reproducibility of the measurement over time, yielding a precision (1σ) of 0.2 wt% C and of 0.03
189 wt% C for the high and the low carbon contents, respectively.

190 The organic carbon content was measured using a modified Walkley Black method (Gras et
191 al., 2017; Walkley and Black, 1934) . Equation (2) below, from De Vos et al (2007) was used to
192 calculate the organic carbon content:

$$\%C_{org} = M \times \frac{(V_1 - V_2) \times 0.3}{W} \times 1.32 \quad (2)$$

193 where M is the molarity of the reference Fe₂SO₄ solution, V₁ is the volume (mL) of Fe₂SO₄ needed
194 in a blank titration, V₂ is the volume (mL) of Fe₂SO₄ consumed in the sample titration, W is the
195 weight (g) of the sample and 1.32 is the correction factor (Chatterjee et al., 2009; Conyers et al.,
196 2011; De Vos et al., 2007).

197 **4. Results**

198 **4.1 Field observations:**

199 The experimental cells are located near Amos, in north-western Quebec, in a continental
200 climate characterized by large differences in temperature between cold winters and warm summers.
201 The mean temperature and the mean solar radiation intensity between the years 2011 and 2016
202 varied respectively, from -18°C and 32 W/m² in winter to 17°C and 230 W/m² in summer (Table 1).
203 During summer, the rainfall events slightly decreased but intense rainfall events occurred frequently
204 (≥30 mm). The mean total annual precipitation (snow and rain) between 2011 and 2016 was 840
205 mm/yr. The recording of rainfall was sometimes disrupted by mechanical failure and was completed
206 using data from Environment Canada.

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4 207 At the bottom of the cells, the leachate flow rate was recorded between April and November
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6 208 using a typing bucket rain gauge. The logging was frequently disrupted due to weather. Figure 3
7
8 209 presents the flow rates recorded between May and August 2013, together with the rain events for
9
10 210 the year. In 2013, following a precipitation event of 25 mm in one day, the maximum flow rate in
11
12 211 EC-1 was ~2000 L/day whereas in EC-2 it was ~1400 L/day (Figure 3). The mean discharge
13
14 212 recorded between 2011 and 2015 ranged from 217 L/day to 546 L/day for EC-1 and from 111 L/day
15
16 213 to 241 L/day for EC-2 (Figure 3)

17 214 In cell EC-1, the grain size of the waste rock is heterogeneous and ranges from silt to pluri-
18
19 215 centimetric blocks whereas material from EC-2 is characterized by a D10 of 2.2 μm , a D80 of 119
20
21 216 μm and a uniformity coefficient ($C_u = D_{10}/D_{60}$) of 22 (Kandji et al., 2017) (Figure 2 a and e). The
22
23 217 mean porosity in cell EC-2 is 44% and the dry bulk density is 1242 $\text{kg}/\text{m}^3 \pm 55 \text{ kg}/\text{m}^3$. Other
24
25 218 hydrogeological parameters for EC-1 and EC-2, presented in Gras et al. (2017), were estimated
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27 219 from the literature (Aubertin et al., 1996; Lechat et al., 2016; Molson et al., 2008, 2005,
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29 220 Peregoedova et al., 2014, 2012).

30 221 Figure 4 presents the evolution of the volumetric water content with depth in EC-2, with
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32 222 total precipitation for the year 2016. During the winter, the water content just below the surface (~ 4
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34 223 cm deep) was constant near 10% whereas at 14 cm and 25 cm depths the water content reached
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36 224 30% and 40 %, respectively. In spring, the water content increased by 10 % throughout the cell and
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38 225 fluctuated with rain events (Figure 4). Between 2011 and 2015, the average water content was ~25
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40 226 % at 4 cm depth in cell EC-2.

41 227 **4.2 Chemical evolution of the leachate water:**

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44 228 Rainwater chemical analyses yielded a pH of 5.5 and contained trace amounts of Al (0.03
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46 229 mg/L), Pb (0.001 mg/L) and Zn (0.03 mg/L). Between December and April, the interstitial waters
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48 230 were frozen, thus chemical analyses on leachate water were performed only from May to
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50 231 November. The leachate analyses from both cells revealed the same pattern of evolution, with a
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52 232 transient phase after construction during the summer of 2011, followed by a regime characterized
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54 233 by seasonal cycles (Figures 5 and 6).

55 234 In EC-1 during the first summer (2011), the magnesium concentration, alkalinity, and pH
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57 235 increased from 6.5 to 110 mg/L (Mg), from 240 to 510 mg/L CaCO_3 (Alk) and from 8.17 to 8.81
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59 236 (pH), respectively (Figure 5 a). During the same period, calcium and silica concentrations decreased
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61 237 from 85 to 36 mg/L and from 7.8 to 3.3 mg/L, respectively (Figure 5 b). Since 2012, the magnesium

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238 and silica concentrations, as well as the alkalinity and pH, varied in seasonal cycles from 125 to 180
239 mg/L (Mg), from 1.2 to 6.2 mg/L (Si), from 125 to 700 mg/L CaCO₃ (Alk) and from 8.1 to 9.7
240 (pH), respectively. During these seasonal cycles, the magnesium concentration, pH and alkalinity
241 decreased while silica concentrations increased from May to August. From August to November the
242 trends were reversed (Figure 5 a,b). The calcium concentration generally decreases from year to
243 year but had the same seasonal variations as silica and ranged from 3.4 to 20 mg/L (Ca).

244 In EC-2, the concentrations of chemical elements were lower than in EC-1 (Figure 6).
245 Between July and November 2011, the magnesium concentration was highly variable, with a
246 minimum and maximum value of 70 and 120 mg/L, respectively. Meanwhile, the alkalinity and pH
247 increased from 45 to 180 mg/L CaCO₃ (Alk) and from 7.64 to 9.45 (pH), respectively (Figure 6 a),
248 whereas calcium and silica concentrations decreased from 85 to 36 mg/L (Ca) and from 7.8 to 3.3
249 mg/L (Si), respectively (Figure 6 b). Between 2012 and 2015, as in EC-1, the magnesium, silica and
250 calcium concentrations, as well as alkalinity and pH, varied seasonally between 50 and 140 mg/L
251 (Mg), 0.9 to 7.2 mg/L (Ca), 0.67 to 2.7 mg/L (Si), 91 to 509 mg/L CaCO₃ (Alk), with a rise in pH
252 from 8.93 to 10, respectively. While seasonal variations were the same as in EC-1, the intensity of
253 seasonal variations in magnesium concentrations and alkalinity has decreased over the years in cell
254 EC-2 (Figures 6 a,b).

255 In both experimental cells, potassium and sodium concentrations decreased from year to
256 year since 2011. Additionally, similar to silica, the potassium and sodium concentrations increased
257 each year between May and July then decreased until November (Figures 5 and 6). The potassium
258 and sodium concentrations ranged from 4 to 2.3 mg/L (K) and from 13 to 2 mg/L (Na), respectively
259 in EC-1, and from 15 to 0.2 mg/L (K) and from 26 to 0.9 mg/L (Na) in EC-2 (Supplementary
260 information). The concentrations of other chemical components were near or below their detection
261 limits (Supplementary information). Finally, in both cells the amplitude of the seasonal cycles
262 seemed to decrease from year to year (Figures 5 and 6).

263 Thermodynamic equilibrium calculations revealed that carbonate saturation indices first
264 increased in 2011 and then evolved seasonally following pH and alkalinity. The calculations
265 suggest that magnesite, calcite and aragonite were over-saturated in leachate water, whereas
266 nesquehonite remained under-saturated in the first 6 months of the experiment following set up in
267 2011 (Figure 7). The saturation indices of aragonite and calcite decreased over the years with
268 calcium concentrations, but the leachate water remained generally over-saturated with respect to
269 these minerals. Between May and July, saturation indices for hydromagnesite and artinite decreased

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270 with the leachate becoming under-saturated whereas during the next three months, saturation
271 indices increased, with the leachate becoming over-saturated in November (Figure 7). The
272 thermodynamic equilibrium calculations also suggest that the partial pressure of CO₂ in the leachate
273 water was often below the atmospheric partial pressure, also fluctuating with seasonal variations.
274 However, the temperature of the leachate water was not measured which reduces precision on the
275 pCO₂ calculations.

276 **4.3 Mineralogical analysis:**

277 XRD analyses of weathered mining residues from both cells revealed the presence of
278 nesquehonite, dypingite, hydromagnesite, aragonite, artinite, and several minerals from the
279 hydrotalcite supergroup, including brugnatellite [Mg₆Fe³⁺(CO₃)(OH)_{13.4}(H₂O)], pyroaurite 3R, and
280 pyroaurite 2H [Mg₆Fe₂³⁺(CO₃)(OH)_{16.4}(H₂O)]. However, owing to the low modal abundance of the
281 carbonate minerals, XRD data did not allow an accurate identification of the hydrotalcite
282 supergroup minerals. Of the 19 samples analysed from EC-1, 10 contained hydromagnesite whereas
283 only one EC-2 sample contained hydromagnesite. Surface samples from EC-2 most often contained
284 dypingite. Well-crystalized, primary calcite [CaCO₃] was also found in rock fragments from EC-1
285 (Gras et al., 2017). Finally, in the first 3 centimeters of the core samples at the center of cell EC-2, a
286 decrease in intensity or an absence of brucite peaks was observed in the XRD patterns of the
287 weathered samples.

288 The SEM observations of weathered samples from EC-1 and EC-2 revealed the texture and
289 habit of the precipitated carbonates (Figure 8). The weathered surfaces of samples from the waste
290 rock cell (EC-1) were entirely (Figure 8 a) to partially (Figure 8 b) covered by carbonate minerals
291 with a lamellar texture similar to the habit of hydromagnesite (Figure 8 c). On the surface of several
292 samples, at the grain surfaces, depressions were filled with carbonate minerals, whereas on the top
293 of the grains some well-crystallized lamellar minerals were observed. Well-crystallized carbonate
294 minerals with the typical texture of aragonite or artinite have also been observed on samples from
295 EC-1 (Figure 8 d). At the surface of EC-2, carbonate minerals cement small grains of tailings
296 (Figure 8 e). Flaky carbonate minerals covered by well-crystalized needle-like minerals were
297 observed on the same serpentine grains (Figure 8 f). Additionally, several crystal sizes of
298 nesquehonite were observed on the same samples which indicate repeated precipitation phases
299 (Figure 8 g). Finally, some samples from EC-2 contain potential microbial mats of fungal hyphae
300 intertwined with carbonate minerals (Figure 8 h).

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4 301 Using samples from cells EC-1 and EC-2, thin sections were impregnated with epoxy under
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6 302 vacuum, in order to preserve the carbonate-matrix interface. The carbonate crusts from EC-2
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8 303 samples were too thin for EPMA analysis. Back Scattered Electron (BSE) imaging of the thin
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10 304 sections from EC-1 revealed different patterns of carbonate coating. The carbonate minerals were
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12 305 observed as: (1) thin layers on the serpentine substrate separated from lamellar minerals by a
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14 306 fracture (Figure 9 a), (2) within fractures cemented by carbonate with mining residue fragments
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16 307 (Figure 9 b) or (3) in complex fractures filled by carbonates and with brucite (Figure 9 c). The
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18 308 minerals at the carbonate-matrix interface had oxygen, magnesium and silica concentrations ranging
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20 309 respectively from 61.9 to 13.8 wt% (O), from 47.1 to 6.7 wt % (Mg) and from the detection limits
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22 310 to 21 wt% (Si). Nickel, calcium and aluminum never exceeded 2.3 wt % whereas the iron was
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24 311 commonly lower than 2 wt% , reading 8 wt% in one grain.

24 312 **4.4 Evolution of the carbon content:**

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26 313 The unweathered mining residues within the experimental cell EC-1 were characterized by
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28 314 a total carbon content of 0.13 wt%, whereas the white crusts, which do not contain primary calcite,
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30 315 had a total carbon content ranging from 0.3 wt% to 4.4 wt% C_{tot} (Gras et al., 2017). In cell EC-1, no
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32 316 evidence of organic carbon was observed, and therefore the total carbon content is equivalent to the
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34 317 inorganic carbon content. In contrast, in cell EC-2, spruce needles and leaf fragments were found at
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36 318 the surface (Figure 2 f) thus the organic carbon content was measured in order to compute the
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38 319 inorganic carbon content. In several samples the organic carbon content was near the detection limit
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40 320 (0.4 wt% C_{org}) (Conyers et al., 2011). Therefore, in samples with a carbon content below 0.4 % C_{org} ,
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42 321 the total carbon was considered to be inorganic carbon (Gras et al., 2017). In EC-2, the unweathered
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44 322 residues had a total carbon content of 0.08 wt%. The crusts sampled at the edge of the cell were
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46 323 characterized by an inorganic carbon content ranging from 0.1 wt% C_{inorg} to 4.0 wt% C_{inorg} (Gras et
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48 324 al., 2017). The samples from the first few centimeters of core samples, at the center of cell EC-2,
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50 325 yielded inorganic carbon contents lower than the carbon content of the unweathered mining
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52 326 residues (Figure 10). This is likely a consequence of measurement errors related to the Walkey-
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54 327 Black method or sample heterogeneity. Moreover, the inorganic carbon content changed according
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56 328 to the month of sampling. Below the first centimeter of depth, the inorganic carbon content
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58 329 decreased quickly from 1 cm to 3 cm depth. Between 2014 and 2015, the inorganic carbon content
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60 330 ranged from 0.15 wt% to 0.43 wt% and was higher in July than in May or October/November. From
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62 331 below 3 cm depth to the bottom of cell EC-2, the inorganic carbon content was constant near
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64 332 0.2 wt% (Gras et al., 2017) (Figure 10). Figure 11 presents the inorganic carbon content measured
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66 333 at the surface of EC-2 since 2011, and a cross-section of cell EC-2 with the spatial distribution of

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334 the inorganic carbon content measured in May 2015. The contours were drawn using linear
335 interpolation between the core samples. The mining residues under the wood plank, at the edges of
336 cell EC-2, (Figure 2 g) had an average inorganic carbon content of 1.08 wt% whereas at the edges
337 of the cell in May 2015, the inorganic carbon content decreased from 0.5 wt % at the surface, to 0.3
338 wt% at a depth of 10 cm.

339 **5. DISCUSSION**

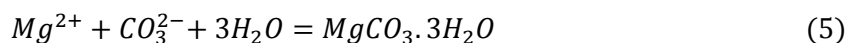
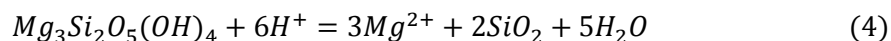
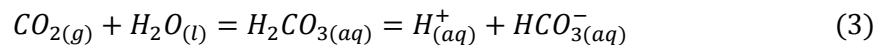
340 Since construction of the experimental cells during the summer of 2011, the mining
341 residues underwent atmospheric weathering. Previous work demonstrated that passive carbon
342 mineralization had indeed induced atmospheric carbon sequestration in the DNP residues (Gras et
343 al., 2017). The main parameters controlling the extent of mineral carbonation include characteristics
344 inherent to the residues such as the mineral composition, surface area, porosity and permeability.
345 Other parameters depend on the environment, such as rain fall frequency, temperature, and relative
346 humidity (Assima et al., 2014c, 2013, 2012; Awoh et al., 2014; Bea et al., 2012; Harrison et al.,
347 2015; Kandji et al., 2017a, 2017b; Pronost et al., 2011; Wilson et al., 2014; Zarandi et al., 2017b,
348 2016). Both experimental cells (EC-1 and EC-2) were filled with ultramafic mining residues from
349 the same nickel deposit. Mining residues in EC-1 and EC-2 therefore had a similar initial
350 mineralogy (Figure 3a-b) where the main minerals were chrysotile, lizardite, brucite, chlorite and
351 magnetite, whereas calcite was found in minor amounts in the waste rock residues (Pronost et al.,
352 2010; 2012; Staples et al., 2013; Gras et al. 2017). The brucite content in the tailing residues of cell
353 EC-2, was approximately 10.2 wt% (Assima et al., 2013). During 4 years of monitored weathering,
354 the residues were submitted to the same conditions of precipitation, temperature and relative
355 humidity variations. However, the hydrogeological characteristics of the mining residues (porosity,
356 water content, tortuosity, permeability), which are specific to each cell, control the flows of gas and
357 water. Cell EC-1 has hydrogeological properties analogous to a heterogeneous gravel-silt, whereas
358 in cell EC-2 the porous medium is similar to that of a silty-clay (Figure 2). On the other hand, the
359 cells contained respectively, approximately 104 tonnes (EC-1) and 5 tonnes (EC-2) of residues and
360 the surface area exposed to rainwater was greater for cell EC-1 (~35 m²) than for EC-2 (~19 m²). As
361 a result, the cell thicknesses are about 2 meters and 35 centimeters, respectively, for EC-1 and EC-
362 2. The liquid-solid ratio and thus also the water content were higher in EC-2 (Figure 4) than in EC-1
363 (Gras et al., 2017). The flow rates measured at the bottom of the cells thus depended on the
364 hydrogeological properties of each cell. After a rain event, an abrupt increase of the flow rate was
365 recorded in both cells (Figure 4). Counter-intuitively to what the hydrogeological properties would
366 suggest, in cell EC-1 the flow rate decreased slowly in the recession curve (Figure 3) whereas in

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367 EC-2 the flow rate decreased more quickly after a rain event. This is best explained by the small
368 amount of mining residues within EC-2. Despite a porous medium similar to a silty-clay, the
369 smaller thickness in EC-2 (35 cm) resulted in a short residence time for water. In EC-1, the
370 residence time of water was longer but did not exceed a few days (Figure 3). In 2013, the flow rate
371 measured at the bottom of EC-1 was higher than in EC-2 which was most likely due to the
372 difference in the surface area exposed to rain. Physical property differences between the two cells
373 may influence the carbon mineralization reactions and, therefore, the carbon sequestration capacity.
374 In the following sections, the observed impacts of atmospheric weathering on leachate water
375 geochemistry will be used to discuss the evolution of carbon mineralization over time and to
376 estimate the amount of atmospheric CO₂ sequestered in the cells.

377 **5.1 Impacts of atmospheric weathering on leachate geochemistry.**

378 In cells EC-1 and EC-2, rainwater in equilibrium with atmospheric CO₂ infiltrates the
379 mining residues and dissolves the magnesium (Mg²⁺) from minerals such as brucite or serpentine.
380 The Mg²⁺_(aq) released into leachate water reacts with interstitial water carbonate (CO₃²⁻) and
381 bicarbonate (HCO₃⁻) ions to form carbonate minerals (Sanna et al., 2014; Harrison et al., 2019),
382 following reactions 3-5 below:



383 Dissolution reactions (3 and 4) and carbonate precipitation (5) are controlled by temperature, pH
384 and solution chemistry, and may also be affected by biological processes (McCutcheon et al., 2016;
385 Power et al., 2013a, 2016, 2010, 2009). In the experimental cells, reactions 3, 4 and 5 occur
386 simultaneously such that the leachate waters collected at the bottom of both cells reflect the
387 equilibrium between these reactions at the times of sampling. From 2011 to 2015, and despite
388 differences in physical properties between the two cells, two regimes can be recognized for leachate
389 water chemistry (Figures 5 and 6). First, a transitional regime in 2011 during which the pH,
390 alkalinity and magnesium concentrations increase in the leachate water whereas silica, calcium,
391 potassium and sodium concentrations decrease. In the second regime, starting in 2012, the pH,
392 alkalinity, Mg, Si, Ca, Na and K concentrations in leachate water show seasonal variations, while
393 the other metal concentrations are stable or below detection (Supporting information). The greater

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394 amount of mining residues and the larger surface area of EC-1 to collect rain, as well as its
395 hydrogeological parameters which are more favourable to water infiltration compared to that of cell
396 EC-2, could explain the higher concentrations observed in cell EC-1 (Figures 5 and 6). However,
397 the concentrations normalized to the volume of mining residues demonstrate that the release rates of
398 different components in EC-1 were lower than in EC-2 (Kandji et al., 2017). The contrast in release
399 rates between both cells may be explained by (1) the finer grain-size and thus a higher specific
400 surface in cell EC-2, and (2) the high liquid-solid ratio in EC-2 (Plante et al., 2014, Kandji et al.,
401 2017). Despite these differences, the same processes appear to control the evolution of the leachate
402 water chemistry in both cells (Figures 5 and 6).

403 **5.1.1 Transitional regime**

404 In July 2011, atmospheric weathering of the mining residues began with acidic meteoric
405 water (pH ~ 5.5) infiltrating the mining residues and dissolving serpentine minerals, brucite and
406 minor amounts of diopside, albite, biotite and calcite (Staples et al., 2013; Pronost et al., 2012,
407 Kandji et al., 2017). The increase of Mg concentration in leachate water was congruent with the
408 dissolution of serpentine minerals, brucite and minor silicate minerals. Dissolution of brucite is
409 further suggested by a decrease of intensity or absence of the XRD peaks of brucite in weathered
410 EC-2 samples. Concurrent to dissolution, H⁺ was consumed through weathering, which caused pH
411 and alkalinity increases in leachate water (Figures 5 and 6) (Kandji et al., 2017b; Lechat et al.,
412 2016; Ulven et al., 2017). Concentrations of Si, Ca, Na or K in leachate water indicate active
413 dissolution of serpentine minerals and silicate minerals such as diopside, albite or biotite. On the
414 other hand, a decrease of Si and other metal concentrations between July and November 2011
415 suggests a lower dissolution rate of serpentine and silicate minerals during this period, which is
416 consistent with the pH increase and a decrease of the abundance of these minerals (Figures 5 and 6).
417 Additionally, the increasing pH may cause incongruent dissolution of serpentine minerals, and a
418 preferential release of Mg over Si (Pokrovsky and Schott, 2000), which supports the observed
419 decrease of Si concentrations from July to November 2011. Brucite was therefore the main but not
420 the only source of Mg in interstitial water of the experimental cells, which is consistent with kinetic
421 tests completed in the laboratory (Kandji et al., 2017). During this transitional regime, the saturation
422 indices of all carbonates increase, and several become over-saturated such as magnesite,
423 nesquehonite aragonite and calcite (Figure 7).

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424 **5.1.2 Seasonal regime**

425 Since 2012, leachate water from cells EC-1 and EC-2 has been characterized by high
426 concentrations of Mg, ranging from 50 to 180 mg/L, and a pH ranging from 8.1 to 10 in which
427 HCO_3^- is the dominant carbonate species (Appelo and Postma 2005). The leachate water from both
428 cells is therefore similar to a Mg- HCO_3^- - type, or type I water, characteristic of open-system
429 interaction between CO_2 -bearing meteoric water and ultramafic rocks (Bruni et al., 2002; Cipolli et
430 al., 2004; Marques et al., 2008; O'Neil and Barnes, 1971; Oskierski et al., 2016; Paukert et al., 2012;
431 Rollo and Jamieson, 2006). Nevertheless, dissolution of CO_2 in interstitial water is the first limiting
432 step of carbon mineralization in the experimental cells (Gras et al., 2017), and the leachate water
433 geochemistry indicates that reactions occur in an open system with atmospheric CO_2 . The pH,
434 alkalinity, and the Si, Mg, Ca, K, and Na concentrations from leachate waters in both cells evolved
435 seasonally while concentrations from other chemical components were stable or below detection
436 (Figures 6 and 7) (Supplementary information). These seasonal variations of leachate geochemistry
437 can be explained by: (1) changes in the hydrologic regime (Nordstrom, 2011, 2009), and (2)
438 changes of the equilibrium conditions between the carbon mineralization reactions (Wilson et al.,
439 2010).

440 Changes in hydrological regimes at mine waste sites over time can have important impacts
441 on water quality (Nordstrom, 2011). During dry periods, for example, the concentration of
442 dissolved metals increases slowly in the leachate water. In contrast, the first strong rainstorm
443 following a dry period (first flush), or an intense rain event, may cause an abrupt increase of
444 concentrations followed by a decrease (Nordstrom, 2011, 2009). The climate near Amos (Quebec),
445 is characterized by large changes in environmental conditions over the year (Table 1). During
446 winter, precipitation is lowest, and the water content in both cells is minimal, near the field capacity
447 and the permanent wilting point. Despite these conditions, carbon mineralization should be effective
448 and carbonates such as landsfordite, could precipitate (Beinlich and Austrheim, 2012; Ulven et al.,
449 2017; Zarandi et al., 2016). Spring snowmelt induces a first flush of water after the relative dry
450 winter period, which was observed in May 2016 as an increase in water content at all depths in cell
451 EC-2. Such a first flush in spring or intense rain events throughout the year may have impacted the
452 leachate water geochemistry and could explain abrupt changes. Each year, the Mg concentrations
453 and alkalinity values tend to be higher in the spring (May and June) and fall (September to
454 November), and lowest in the summer (July and August). These trends are inverse with that of
455 precipitations. It thus seems that Mg concentrations and alkalinity values (related to DIC) might be
456 controlled, at least in part, to dilution from rain and snowmelt water.

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457 Every year, between May and July, the temperature and solar radiation increased, while from
458 August to October a decrease was observed. The relative humidity in the atmosphere and total
459 precipitation were slightly lower from May to July than between August to October. Additionally,
460 during the summer, rain events were slightly less frequent (Figures 5 and 6) (Table 1). Decreasing
461 rainfall events between May and July caused a deficit of water in the cells, over a period during
462 which temperature and solar radiation were conducive to evaporation. During this period, a
463 decrease in water content at 4 cm depth in EC-2 was observed in 2013 and 2014. Similarly, between
464 the end of July and November of each year, increases in precipitation caused ingress of water within
465 the cells and in 2016, the water content at 4 cm depth increased in cell EC-2 (Figure 4 and Table 1).

466 Potassium and sodium ions react little during transport in the experimental cells and are
467 thus considered conservative in this study. Furthermore, these elements were not affected by
468 changes in equilibrium of the carbon mineralization reactions. During dry seasons (May to July),
469 when evaporation was highest, K, Na, Si and Ca concentrations increased. In contrast, when
470 precipitation then increased (August to November), concentrations of K, Na, Si, Ca, decreased.
471 Changes in the hydrological regimes over the year then impacted leachate water quality in the DNP
472 residues. However, the decrease of magnesium concentrations during this seasonal regime, is not
473 directly correlated with changes in precipitation and evaporation conditions, and is not yet fully
474 understood.

475 Changes in evaporation conditions and in watering may alter the equilibrium between the
476 three principal reactions of carbon mineralization presented earlier: (3) dissolution of CO₂ in water,
477 (4) dissolution of reactive minerals, and (5) carbonate precipitation (Assima et al., 2012; Kandji et
478 al., 2017b; Wilson et al., 2014; Zarandi et al., 2017b). Dissolution of CO₂ in interstitial waters
479 contributes to the dissolved inorganic carbon which produces bicarbonate (HCO₃⁻) and carbonate
480 (CO₃²⁻) ions. Reaction 4 releases magnesium ions in the interstitial water, while reaction (5)
481 consumes magnesium ions and bicarbonate ions. Changes in climatic conditions and precipitation
482 could promote one of these three reactions over the others and induce disequilibrium which in turn
483 would modify the leachate water geochemistry (Beinlich and Austrheim, 2012; Wilson et al., 2010).

484 From year to year, the intensity of the seasonal cycles in Mg concentrations and alkalinity
485 seems to decrease, particularly in cell EC-2, while the pH slightly increases (Figures 5 and 6). This
486 long-term evolution could be related to a decrease of carbonate precipitation over the years. Indeed,
487 Gras et al. (2017) demonstrated that, since 2012, the decrease in CO_{2(g)} consumption capacity of
488 cells EC-1 and EC-2 was associated with the decrease in brucite content near the surface and due to

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489 surface passivation (Assima et al., 2012; Harrison et al., 2015; Zarandi et al., 2016). Near the
490 surface, a decrease of magnesium in the leachate waters, related to the smaller proportion of brucite,
491 may limit the precipitation of carbonates (which would otherwise be promoted by evaporation) and
492 might explain the long-term geochemical evolution (Figures 5 and 6). Furthermore, a decrease of
493 porosity near the surface, caused by carbonate precipitation, may also alter the carbon
494 mineralization reactions which would also impact the leachate water geochemistry from year to
495 year (Acero et al., 2007; Beinlich and Austrheim, 2012). Further investigations are needed to
496 confirm and understand the long-term evolution of leachate water geochemistry.

497 In summary, results have shown that leachate water geochemistry from the experimental
498 cells EC-1 and EC-2 was influenced by (1) the local weather (temperature, relative humidity, and
499 precipitation) and (2) evolution of the equilibrium between the governing carbon mineralization
500 reactions, leading to an increase of carbonate precipitation.

501 **5.2 Carbonate precipitation**

502 The evolution of leachate geochemistry presented in the previous section influences the
503 carbonate precipitation reactions. Thermodynamic equilibrium calculations reveal that, despite the
504 differences between cells EC-1 and EC-2, the saturation indices of the carbonate minerals have
505 been similar since 2011. However, the saturation indices evolve following seasonal changes of pH,
506 alkalinity and Mg concentrations (Figure 7). The saturation indices of all carbonate minerals first
507 decreased between May and July, then increased until November. Despite these variations, calcite,
508 aragonite and magnesite were over-saturated, since 2011, in leachate water from both cells.
509 Notwithstanding the oversaturation, Ca concentrations were not affected by the increase of
510 carbonate precipitation between May and July. The leachate waters from EC-1 and EC-2 were
511 characterized by high Mg concentrations which can inhibit calcium carbonate precipitation
512 (Hopkinson et al., 2008). Inhibition of calcium carbonate precipitation can explain why Ca
513 concentrations did not change over seasonal cycles and is further consistent with the low modal
514 proportion of neo-formed calcium carbonates observed in this study and by Gras et al., (2017).
515 Saturation indices of artinite and hydromagnesite reflected either over- or under-saturated
516 conditions, whereas nesquehonite was undersaturated (Figure 7). It is important to note that
517 evaporation of leachate water, which may significantly increase the carbonate saturation indices,
518 was not considered here. Oskierski et al. (2016), for example, demonstrated that evaporation of 20%
519 of the leachate water from the Woodsreef mine induced oversaturation for hydromagnesite. At the
520 surface of the cells, where evaporation was highest, the carbonate minerals were therefore most

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521 likely over-saturated. Nevertheless, changes in leachate water geochemistry, between May and July,
522 decreased the carbonate mineral saturation indices and thus these carbonate minerals became under-
523 saturated deeper within the cells. The increase in carbonate precipitation between May and July,
524 which altered the leachate water geochemistry, therefore created a feed-back loop limiting the
525 carbon sequestration potential of the cells.

526 In experimental cells EC-1 and EC-2, the neo-formed carbonate minerals trap atmospheric
527 CO₂ (Gras et al., 2017). In surface samples from both cells, artinite, nesquehonite, dypingite, and
528 hydromagnesite were observed, with rare aragonite. The amount of bound carbon depends on the
529 specific mineral. Nesquehonite has a ratio of CO₂ to Mg of 1, whereas the ratio is 4/5 for
530 hydromagnesite and dypingite. The stability of magnesium carbonate minerals increases from
531 lansfordite and artinite to nesquehonite, then dypingite, hydromagnesite, and stable magnesite,
532 (Canterford et al., 1984; Hopkinson et al., 2008; Langmuir, 1965). At temperatures above 25°C,
533 hydrous-carbonates can evolve from lansfordite to nesquehonite (Beinlich and Austrheim, 2012;
534 Hopkinson et al., 2008), whereas nesquehonite can be converted to dypingite and hydromagnesite
535 during associated wetting/drying cycles and increasing temperature (Hopkinson et al., 2008;
536 Oskierski et al., 2016; Power et al., 2009; Wilson et al., 2009; Zarandi et al., 2017b).
537 Hydromagnesite was more common in samples from EC-1, whereas in EC-2 the main carbonate
538 was dypingite. In cell EC-1, the blocks of waste rock which were more conducive to wetting/drying
539 cycles and evaporation, were coated with carbonate minerals. Conversion from the less stable
540 phases (artinite, nesquehonite) to hydromagnesite was favoured in cell EC-1 which can explain the
541 higher proportion of hydromagnesite in EC-1. In contrast, the finer grain size of the tailings in cell
542 EC-2 maintains a higher water content (Figure 4), which may slow the rate of dehydration of
543 nesquhenotite to hydromagnesite. Fungi at the surface of cell EC-2 (Figures 8 h) could also promote
544 precipitation of dypingite (McCutcheon et al., 2016; Power et al., 2010, 2009). The grain size of the
545 mining residue may therefore influence the type of carbonate minerals precipitated, whereas
546 evaporation and wetting-drying cycles control the conversion. Clearly, the hydrogeological
547 conditions can therefore also influence the quantity of carbon trapped in the residues. In deeper EC-
548 2 samples, however, only hydrotalcite supergroup minerals formed (Supplementary information).
549 As described in previous studies, in both cells EC-1 and EC-2, for example, hydrotalcite supergroup
550 minerals had formed during atmospheric weathering (Gras et al., 2017; Oskierski et al., 2016;
551 Turvey, 2015; Turvey et al., 2017). These minerals precipitated rapidly after exposure to the
552 atmosphere through weathering of brucite under CO₂ - limited conditions (McCutcheon et al., 2016;
553 Mumpton and Thompson, 1966; Turvey et al., 2017).

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554 In cell EC-1, carbonate coatings may also have contributed to surface passivation (Figures 2
555 c, d and 8 a,b) (Assima et al., 2012; Zarandi et al., 2017b), whereas in cell EC-2, the carbonates
556 cemented the tailing grains, causing a decrease in porosity and permeability (Acero et al., 2007)
557 (Figures 2 h and 8 e). Therefore, precipitation of carbonates within the cells may decrease
558 atmospheric CO₂ consumption. In order to characterize the carbonate matrix interface, EPMA
559 analysis was used on waste rock samples from EC-1. In order to identify the minerals at the
560 carbonate-matrix interface, chemical analyses and theoretical mineral compositions have been
561 plotted on ternary diagrams (Figure 9). Most often, the carbonate-matrix interface is sharp and the
562 chemical composition changed from serpentine to carbonates or brucite (Figure 9 c). However, on
563 several samples the chemical compositions of minerals at the carbonate-matrix interface range from
564 the pole of serpentine to a magnesium pole depleted in silica which corresponds either to brucite or
565 carbonates (Figure 9 a,b). Because the EPMA beam size (10 μm) is in some places larger than the
566 target minerals, superposition of serpentine or epoxy and carbonates may have altered the signal to
567 the measured composition. Nevertheless, the range of composition from the pole of serpentine to
568 the magnesian pole is consistent with the incongruent dissolution of serpentine in high pH water, in
569 which Si will be preferentially released over Mg (Pokrovsky and Schott, 2000; Ruiz-Agudo et al.,
570 2012).

571 The EPMA analyses did not allow precisely identifying the carbonate minerals in the mining
572 residues. In addition, the BSE images revealed that carbonate minerals at the surface were fragile
573 (Figure 9 a) and filled the fractures at the expense of brucite (Figures 9 b and c). Frost cycles and
574 dehydration of the carbonate minerals increased the fracturing of waste rock fragments and thus the
575 carbonate coating may have been peeled off (Beinlich and Austrheim, 2012; Ulven et al., 2017;
576 Zarandi et al., 2017b, 2016). Carbonate precipitation therefore contributes to (1) exposure of fresh
577 serpentine to weathering, which maintains atmospheric CO₂ sequestration, and (2) increased surface
578 passivation, which may decrease atmospheric CO₂ consumption. Carbonate precipitation dynamics
579 in the DNP residues, which changed leachate water geochemistry, thus decreased porosity and
580 permeability, promoted fracturation of the mining residues and caused surface passivation, creating
581 a feed-back loop limiting the carbon sequestration potential.

582 **5.3 Quantification of atmospheric CO₂ sequestration**

583 Carbon sampling of cell EC-1 was limited to surface samples, and therefore it was not
584 possible to accurately quantify the carbon sequestered. However, extensive sampling at the center

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4 585 and at the edges of cell EC-2 allowed tracking the evolution of carbon sequestration over time and
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6 586 thus allowed estimating the quantity of captured CO₂.

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9 587 At the center of cell EC-2, the inorganic carbon content increased slowly from year to year
10 588 (Gras et al., 2017) but changed seasonally. Most notably, the carbon content was higher in summer
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12 589 than in autumn or spring (Figure 10). Dissolution of less stable neo-formed carbonate minerals
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14 590 during rain events (Ulven et al., 2017) or changes in water geochemistry (Figures 5 and 6) may
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16 591 have led to these seasonal variations of the carbon content. However, the cores were randomly
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18 592 sampled at the center of the cell, irrespective of surface mineralization, and carbon mineralization at
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20 593 the surface of the cell was not continuous or homogeneous as shown by an evaporitic crust and
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22 594 cones (Figures 2, and 11). In addition, the carbonate crusts were thin and fragile and might have
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24 595 been disturbed over time (Figure 2 h). The small seasonal variations might therefore be an artifact
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26 596 induced by the sampling process. Additional analyses are necessary to better understand the annual
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28 597 evolution of the carbon content in experimental cell EC-2.

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30 598 The inorganic carbon content in cell EC-2 also varied laterally. At the center of the cell, for
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32 599 example, the carbon content was lower and the carbonation front shallower than at the edges of the
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34 600 cell (Figure 11). The water content, at the center of cell EC-2 was near 25 % at 4 cm depth since
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36 601 2011, but below this depth the water saturation reaches 25 to 40 % (Figure 4). Since the mean
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38 602 porosity of the tailings in cell EC-2 was 44%, the residues were therefore almost fully saturated
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40 603 below 4 cm depth. Towards the edges the residue thickness decreases, and the impact of
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42 604 evaporation became gradually more important such that mean water content became lower.
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44 605 Previous studies have shown that high and low water saturations tend to reduce the carbon
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46 606 mineralization reaction rates (Assima et al., 2013, 2012; Awoh et al., 2014; Harrison et al., 2015).
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48 607 In cell EC-2, the watering frequency corresponds to actual rainfall events and thus was the same at
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50 608 the center and the edges of the cell. Carbon mineralization was thus more efficient near the edges of
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52 609 the cell because of the lower water saturation compared to the center of the cell. Similarly, under
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54 610 the wood plank (Figure 2 g), the residues are partially protected from rain fall and the water content
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56 611 was lower, thus carbon mineralization was likely more efficient yielding a higher carbon content
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58 612 (Figures 2 e and 11). In contrast, the capture of carbon near the center of cell EC-2 was inhibited by
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60 613 the higher water content in the mining residues. Alternatively, sheltering from rain by the wood
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62 614 plank may have prevented carbonate dissolution, as argued by Ulven et al. (2017)

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65 615 The quantity of CO₂ sequestered within the experimental cell EC-2 was estimated using the
66 616 measured inorganic carbon content. The carbon of the core samples was weighted by the mass of a

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617 layer using the thickness of the core sample. For the three upper layers, two-thirds of the volume
618 was ascribed to the central core, and one-third to the core from the edge of the cell (Figure 11).
619 With this approach, up to May 2015, an estimated 13 kg of atmospheric CO₂ was sequestered by the
620 mining residues in cell EC-2, which corresponds to a mean rate of 1.4 (+/-0.3) kgCO₂/tonne/year.
621 This rate is about twice as high as the rate calculated by Bea et al., (2012) using numerical
622 simulations for tailing pounds near Mount Keith (Australia). The DNP residues, however, are
623 characterized by a higher brucite content (10.2 vol%) (Assima et al., 2012) compared to the tailings
624 of the Mount Keith mine (2.5 vol%). Brucite is a key mineral which reacts quickly during carbon
625 mineralization and controls its extent (Assima et al., 2013; Pronost et al., 2012; Harrison 2013,
626 2015, 2016, 2017; Kandji et al., 2015). It is therefore likely the higher brucite content in the DNP
627 residues may have induced the higher sequestration rate. The DNP mine will generate, each year,
628 approximately 15 Mt of tailings and release about 127,700 tonnes of CO₂ (Staples et al., 2013;
629 Kandji et al., 2017b). Using the sequestration rate of the experimental cell EC-2, the tailing residues
630 will sequester about 21 kt of atmospheric CO₂ each year, which represents around 16% of the CO₂
631 emitted. This rate of sequestration is lower than the rate calculated from laboratory kinetic tests (8.5
632 kgCO₂/tonne) (Kandji et al., 2017). The contrast between laboratory and natural conditions may be
633 explained by differences in precipitation/watering and climatic conditions (Temperature, RH).
634 Additionally, the experimental cell EC-2 was frequently flooded after intense rain events and during
635 the summer's drought cracks were observed. These extreme water contents limited the carbonation
636 of the residues and may explain the difference between the laboratory and experimental cell tests. In
637 cell EC-1, the hydrogeological properties, which control the fluid flow and influence the mineral
638 carbonation, are different than in EC-2. In addition, the hydrogeological properties are very
639 heterogeneous (Aubertin et al., 1996). Therefore, the results from EC-2 cannot be easily
640 extrapolated, and the estimated amounts of CO₂ capture might be quite different from the real
641 amounts sequestered (Awoh et al., 2014; Lechat et al., 2016).

642 **6. CONCLUSION**

643 Two experimental cells were used to study impacts of atmospheric weathering on passive
644 carbon mineralization in mining residues from the Dumont Nickel Project. The mining residues
645 filling the experimental cells had a similar mineralogy and were submitted to the same weather
646 conditions (temperature, RH, precipitation). However, the hydrogeological properties, which
647 influence the supply of CO₂ and the water content of the cells, were different. Despite these
648 hydrogeological differences, the same processes control the evolution of leachate water
649 geochemistry. High magnesium concentrations and a moderate to alkaline pH characterize the

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650 leachate water from both cells, which is consistent with weathering of ultramafic rocks in a system
651 open to CO₂. Seasonal variations of leachate water geochemistry are caused by (1) seasonal and
652 longer-term changes in rainfall and weather conditions, and (2) a displacement of the equilibrium
653 between the carbon mineralization reactions. Between May and July each year, leachate water flows
654 in a CO₂-depleted environment where supply of atmospheric CO₂ to water is limited (Gras et al.,
655 2017). During this period, evaporation is at its maximum, therefore precipitation of carbonate
656 minerals increases causing a decrease in magnesium concentration and alkalinity. Seasonal
657 variations in leachate water geochemistry also impact the saturation indices of carbonate minerals.
658 Between May and July, hydromagnesite and artinite become under-saturated which limits carbon
659 sequestration. Furthermore, carbonate precipitation, self-limits carbon sequestration through a
660 negative feed-back loop.

661 Over the years, magnesium concentrations and alkalinity decrease which is related to a
662 decrease of CO₂ consumption (Gras et al., 2017). In experimental cells EC-1 and EC-2, carbonate
663 precipitation is mainly driven by evaporation. Dehydration of nesquehonite to hydromagnesite is
664 promoted by the larger grain size in EC-1 and dypingite is more common in EC-2. Since the
665 hydrogeological properties of EC-2 are similar to a silty-clay porous medium, a high liquid/solid
666 ratio is maintained, and residues are nearly saturated at shallow depths which limits carbonate
667 precipitation. Approximately 13 kg (+/- 1) of atmospheric CO₂ were sequestered in cell EC-2
668 between 2011 and 2015, which corresponds to a mean rate of 1.4 (+/-0.3) kgCO₂/tonne/year.
669 However, the carbon sequestration capacity was inhibited by the high water content.

670 This study underlines the critical impact of hydrogeological properties and leachate water
671 geochemistry on atmospheric CO₂ sequestration capacity of ultramafic mine wastes. Changes in
672 these properties during passive carbon mineralization must be addressed in order to optimise
673 atmospheric CO₂ sequestration in large-scale mining waste deposits.

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947 **Figure captions**

948 **Figure 1** : a) Site location and b) geological context of the proposed DNP mine site and
949 Dumont sill.

950 **Figure 2** : Textures in the experimental cells EC-1 and EC-2. a) General view of waste-
951 rock cell EC-1 with pluri-centimetric blocks at the surface, b) white crusts coating surfaces
952 and fractures in samples from EC-1, c) surface of a pluri-centimetric block in EC-1 coated
953 with white crusts, d) white crust observed with binocular magnifier, with several phases of
954 precipitation visible, e) general view of the tailings cell EC-2, f) evaporitic structure (cones)
955 observed at the edges of cell EC-2, g) residues cemented and covered with white crust
956 below the wood support beam at the edges of cell EC-2, h) indurated flat crust, sampled at
957 the edge of cell EC-2.

958 **Figure 3** : Evolution of water flux at the bottom of the experimental cells in 2013.

959 **Figure 4** : Water content evolution with depth in EC-2 and rainfall in 2016.

960 **Figure 5** : Evolution of chemical composition of leachate in EC-1 since 2011.

961 **Figure 6** : Evolution of chemical composition of leachate from EC-2 since 2011.

962 **Figure 7** : Evolution of saturation indices of the main carbonate minerals.

963 **Figure 8** : Scanning electron micrographs of surface samples from EC-1 and EC-2. a)
964 Surface of a white crust sampled in cell EC-1; depressions are filled with fissured

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965 carbonates whereas on the top well-crystalized carbonates are visible, b) serpentine grain,
966 from cell EC-1, partially covered with flaky carbonate minerals, c) white crust, from cell
967 EC-1, with well-crystalized hydromagnesite, d) needle of well-crystalized aragonite
968 observed on sample surface from EC-1, e) surface of a flat crust, from EC-2. Carbonate
969 minerals have coated the surface and cemented the tailings grains. f) Serpentine grain, from
970 flat crust in EC-2, partially covered with flaky carbonates overcome by well-crystalized
971 nesquehonite, g) different sizes of nesquehonite crystals observed on a surface sample from
972 EC-2, h) intergrowth of fungi and carbonate minerals observed at the surface of cell EC-2.

973 **Figure 9** : Back-scattered electron micrographs of polished thin sections from cell EC-1
974 and EPMA chemical compositions reported on ternary diagrams.

975 **Figure 10** : Inorganic* carbon content at the center of cell EC-2

976 **Figure 11** : Cross-section of cell EC-2 in May 2015 and contoured inorganic carbon
977 content.

Figure 1
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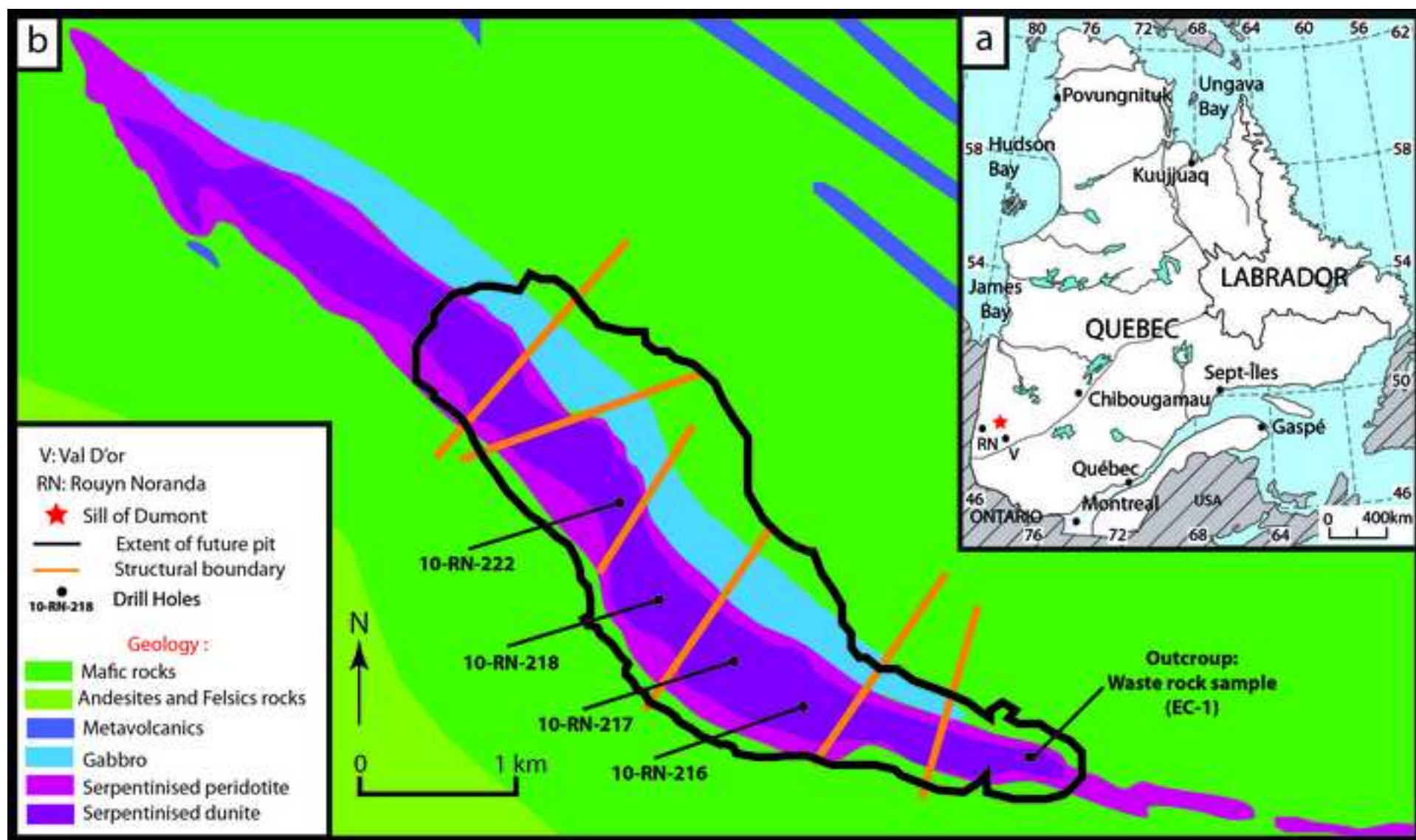


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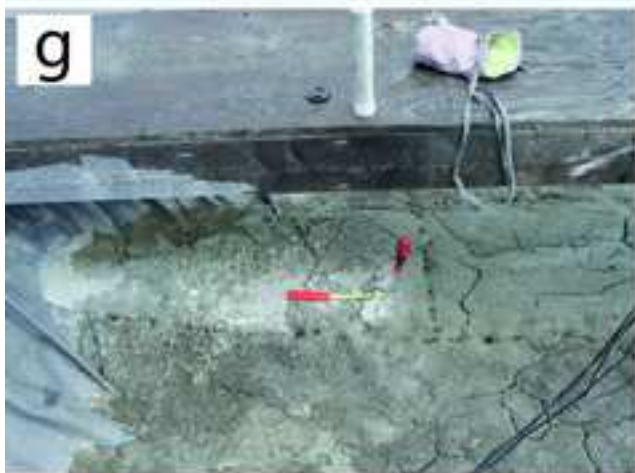
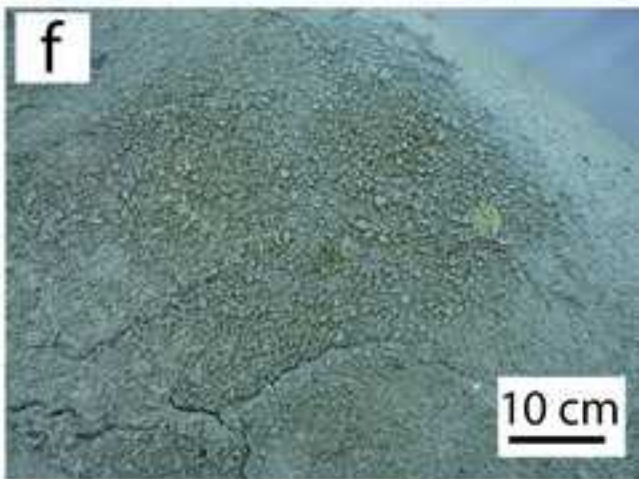
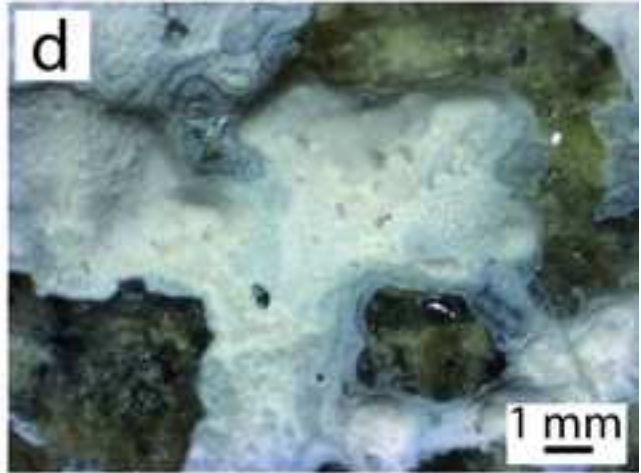
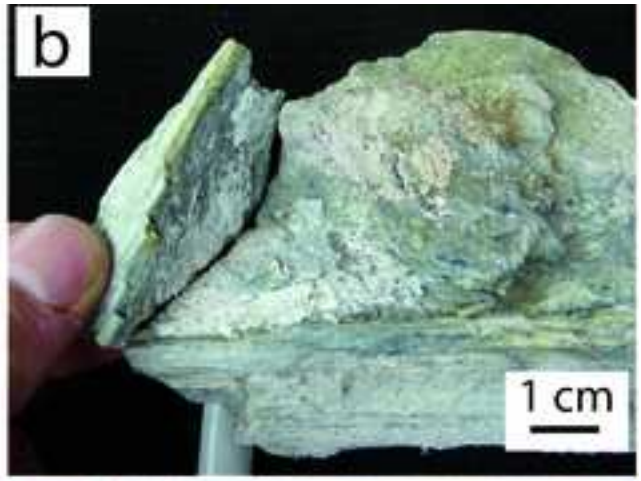


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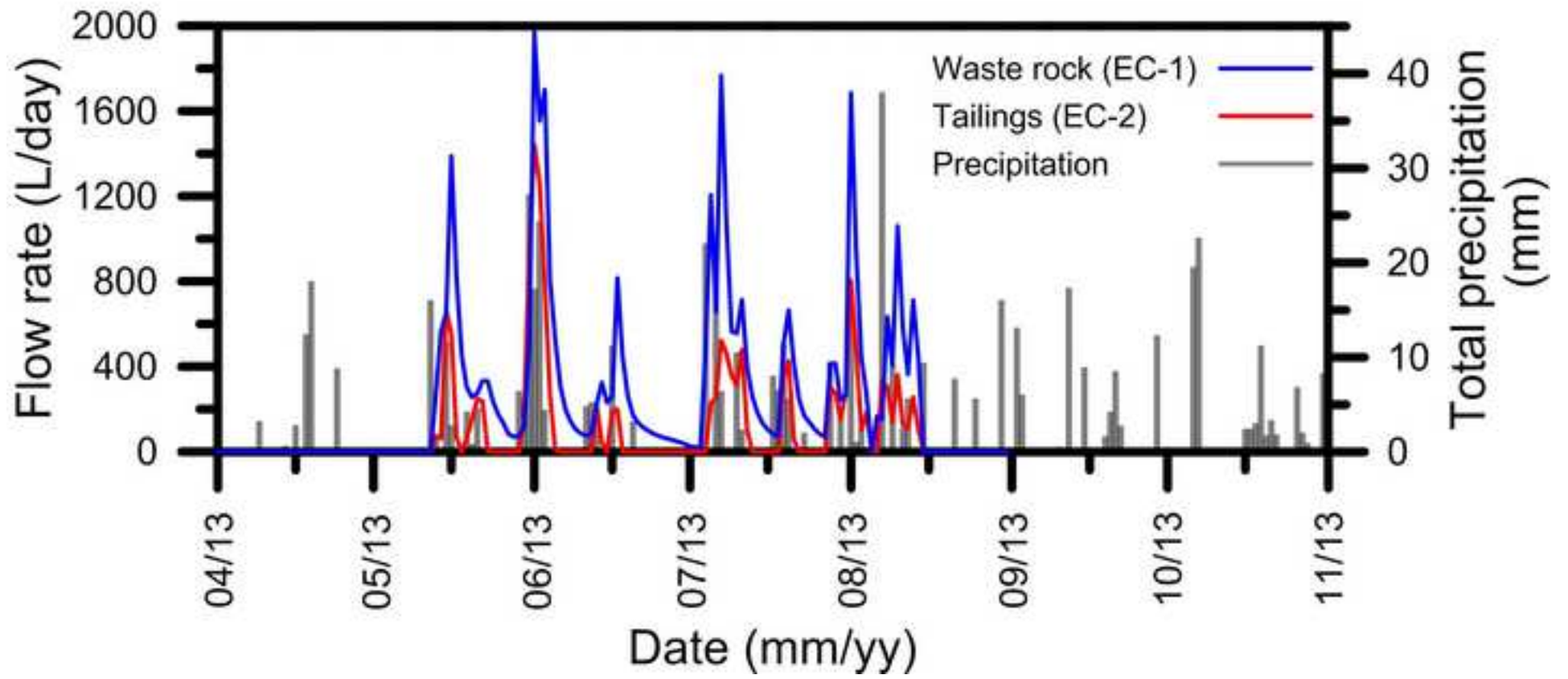


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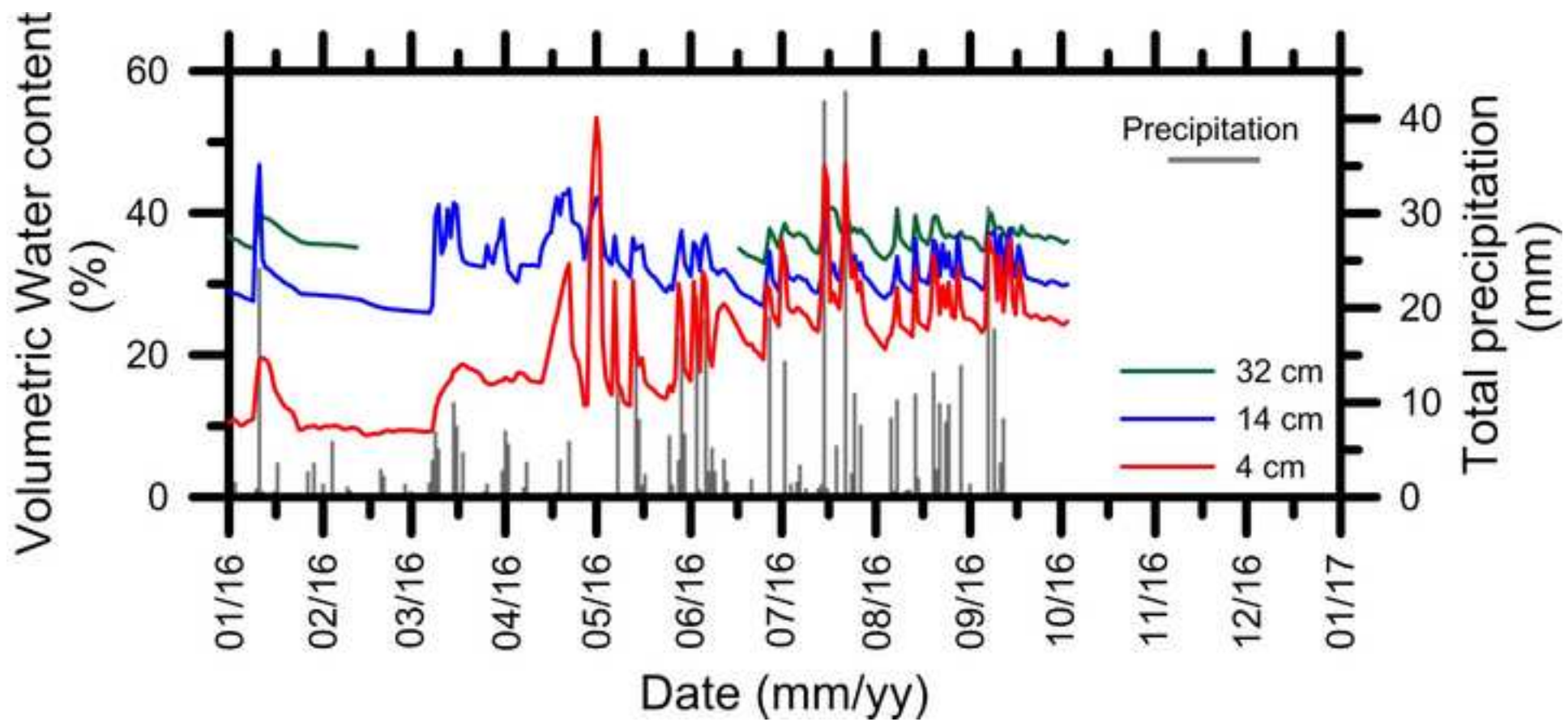


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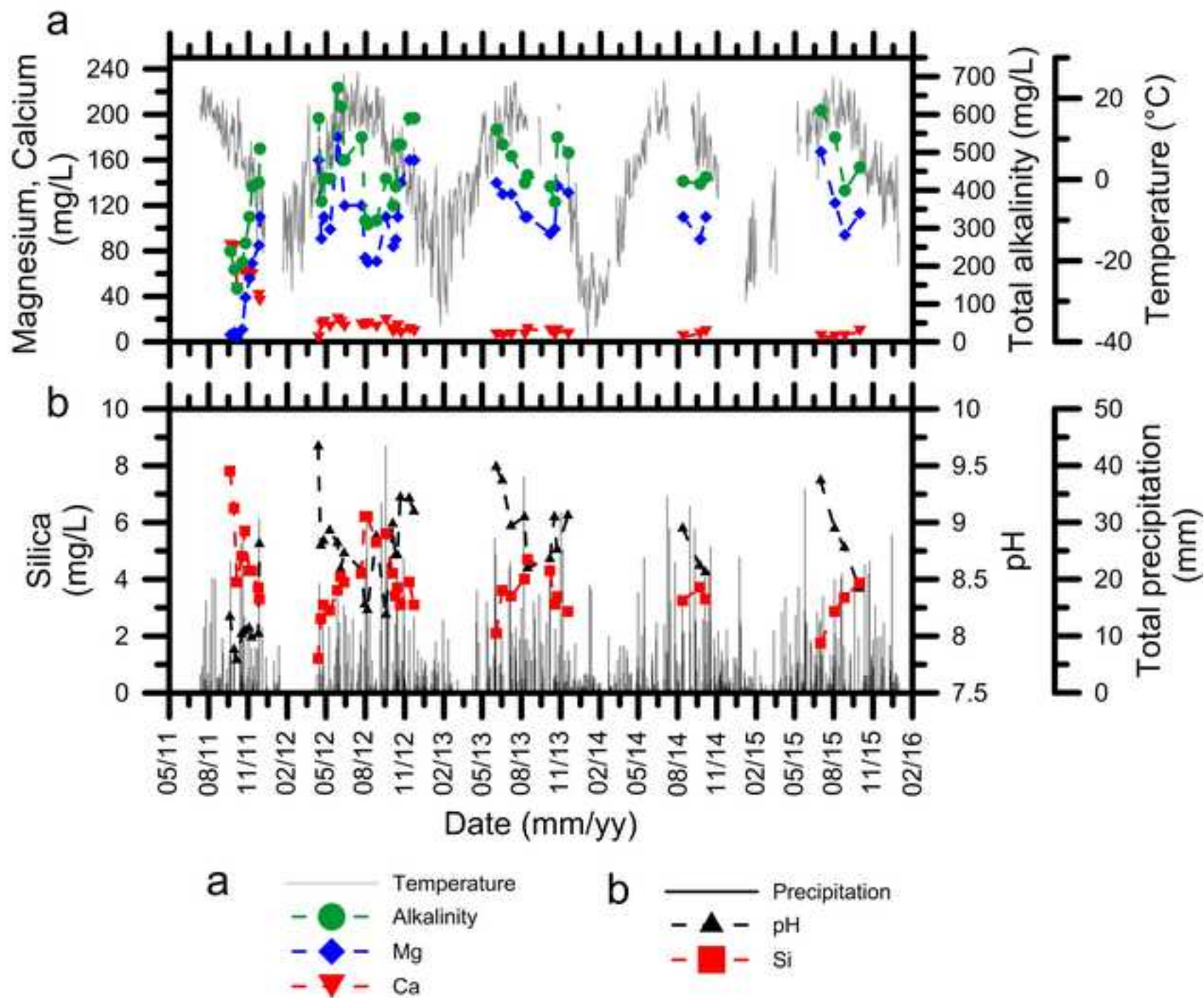


Figure 6
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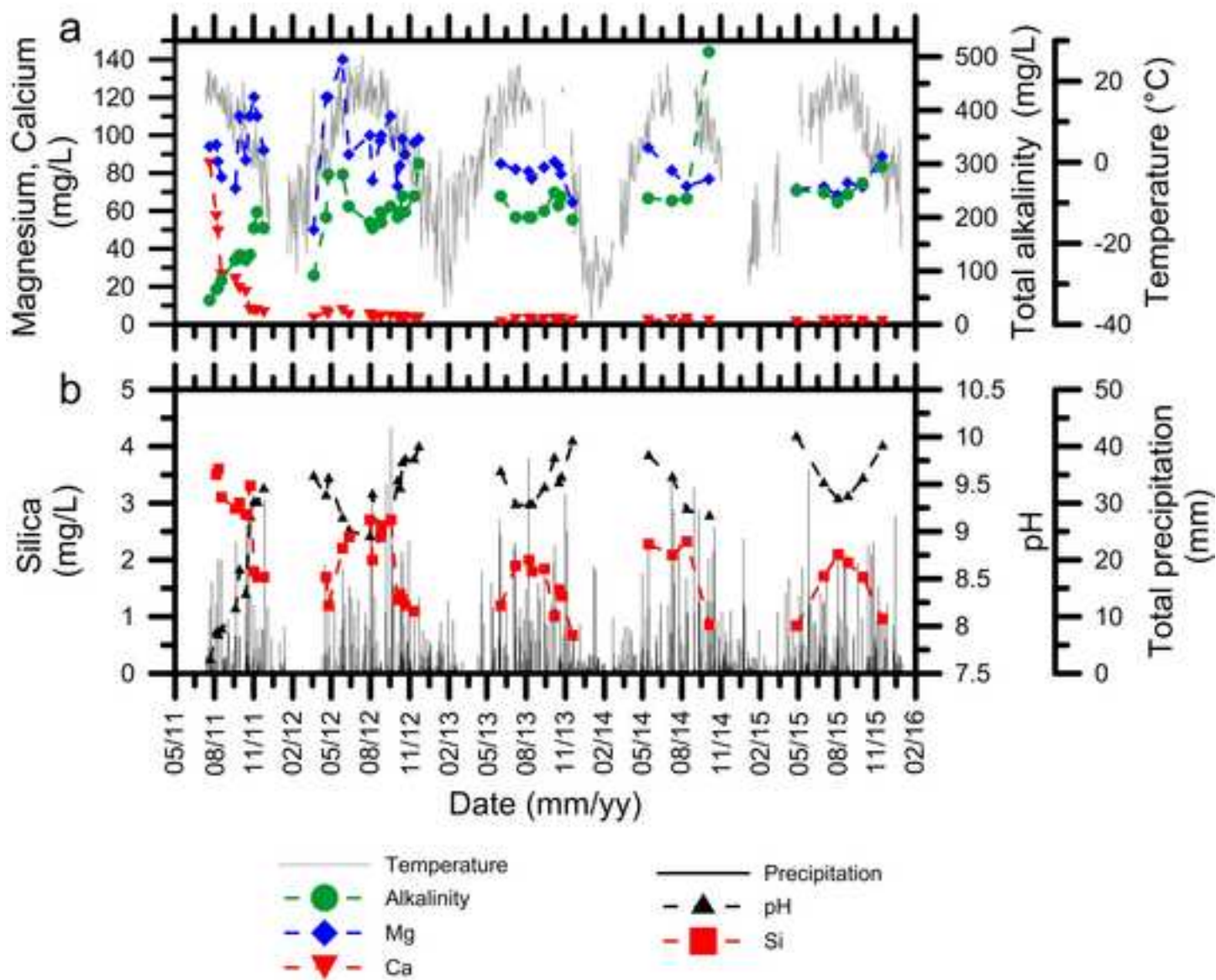
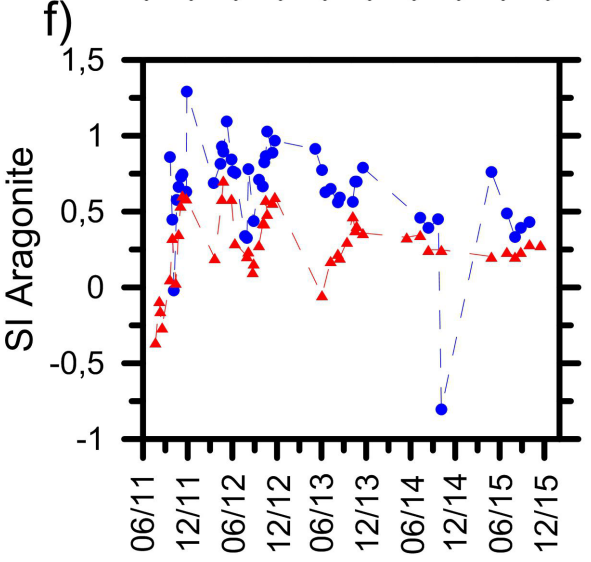
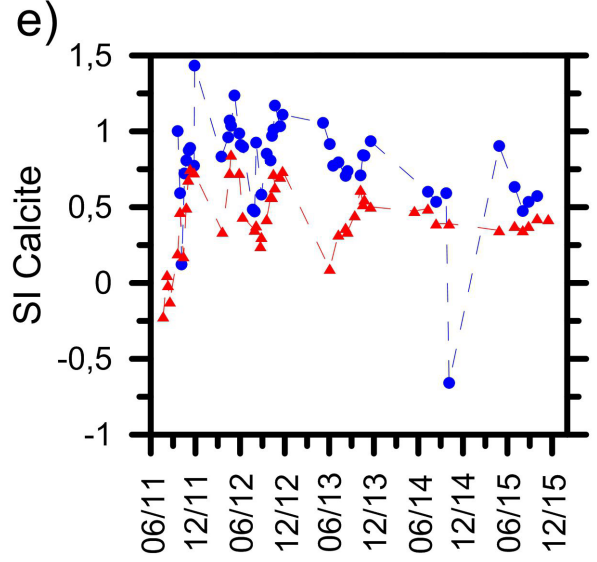
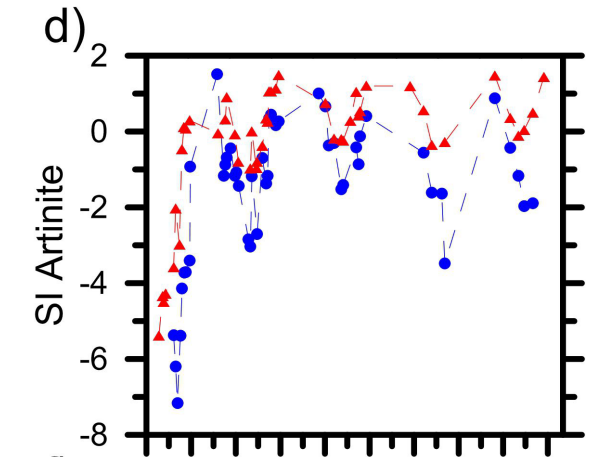
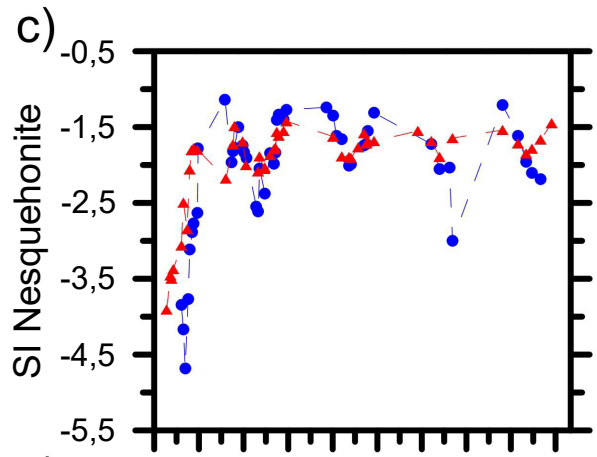
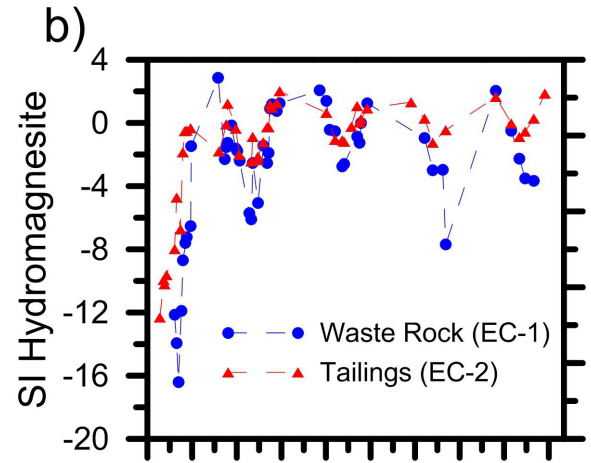
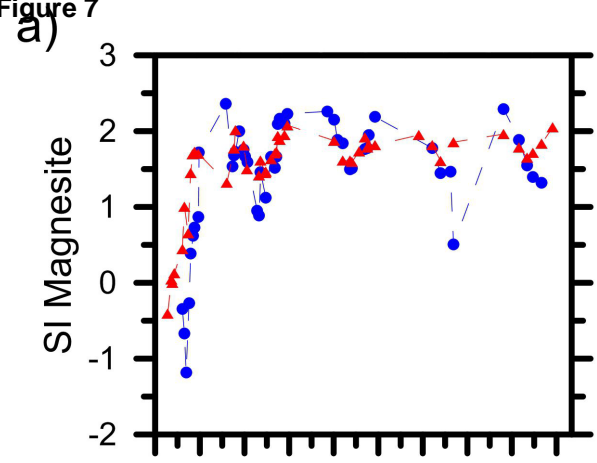


Figure 7



06/11 12/11 06/12 12/12 06/13 12/13 06/14 12/14 06/15 12/15

06/11 12/11 06/12 12/12 06/13 12/13 06/14 12/14 06/15 12/15

Figure 8

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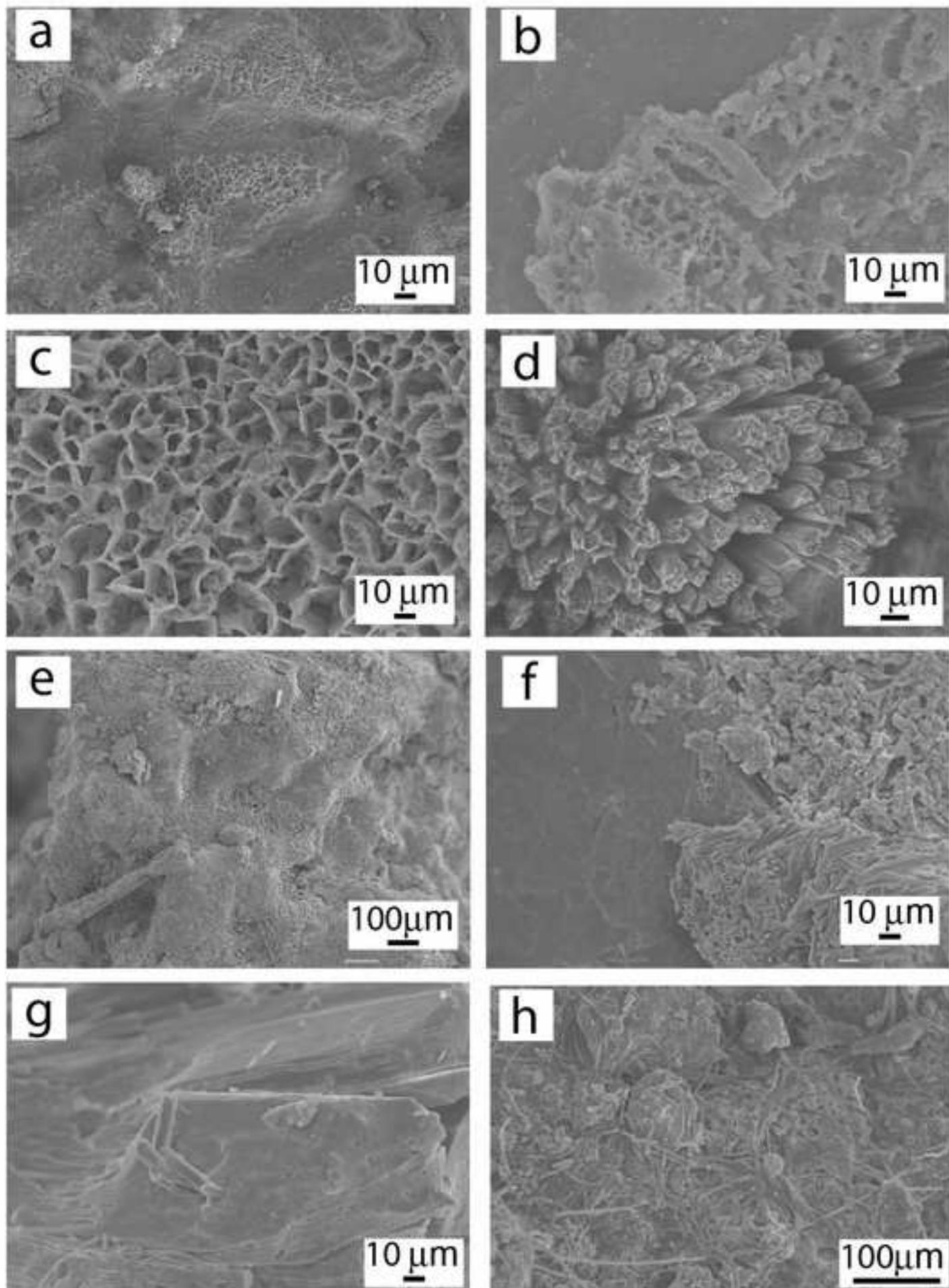
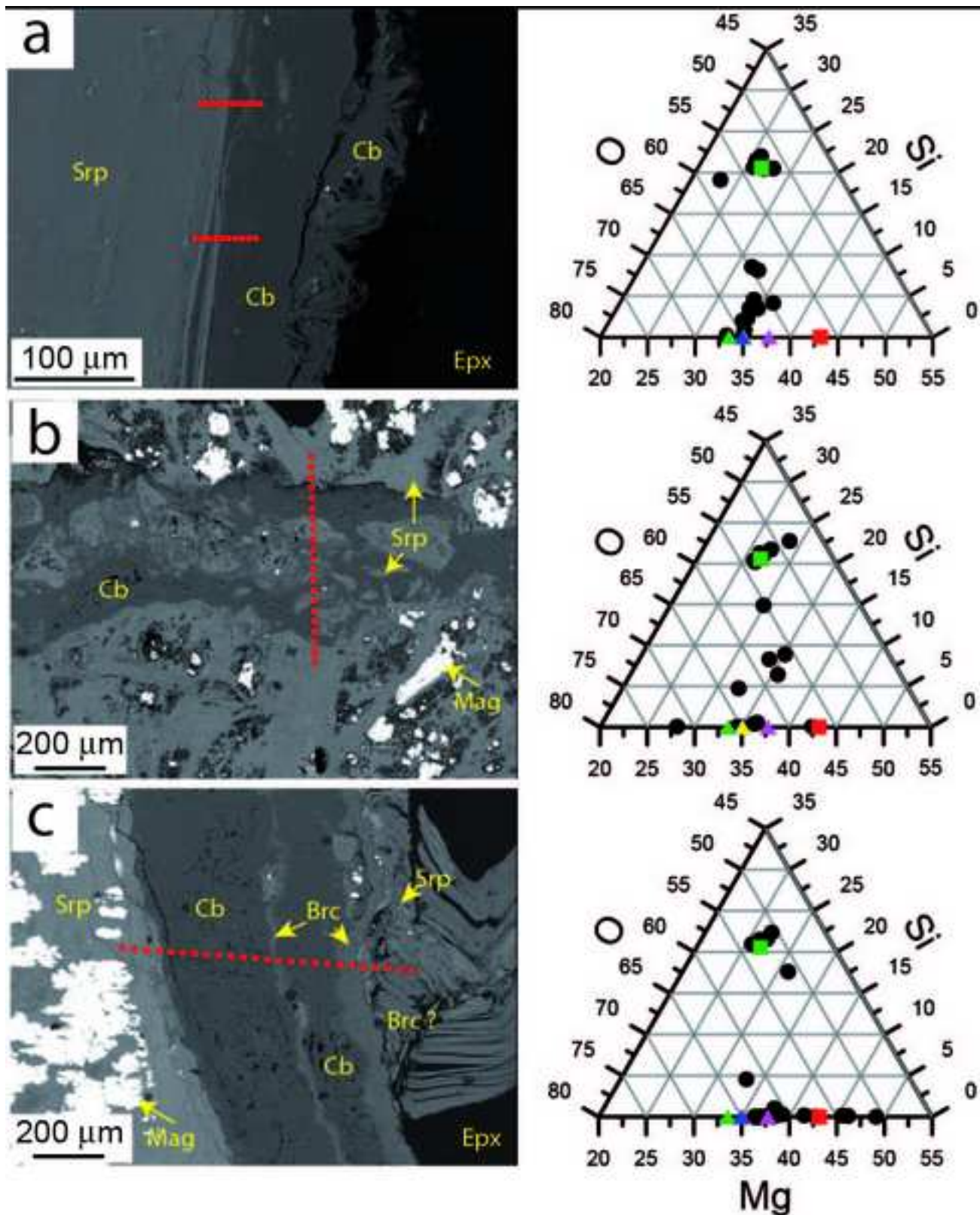


Figure 9
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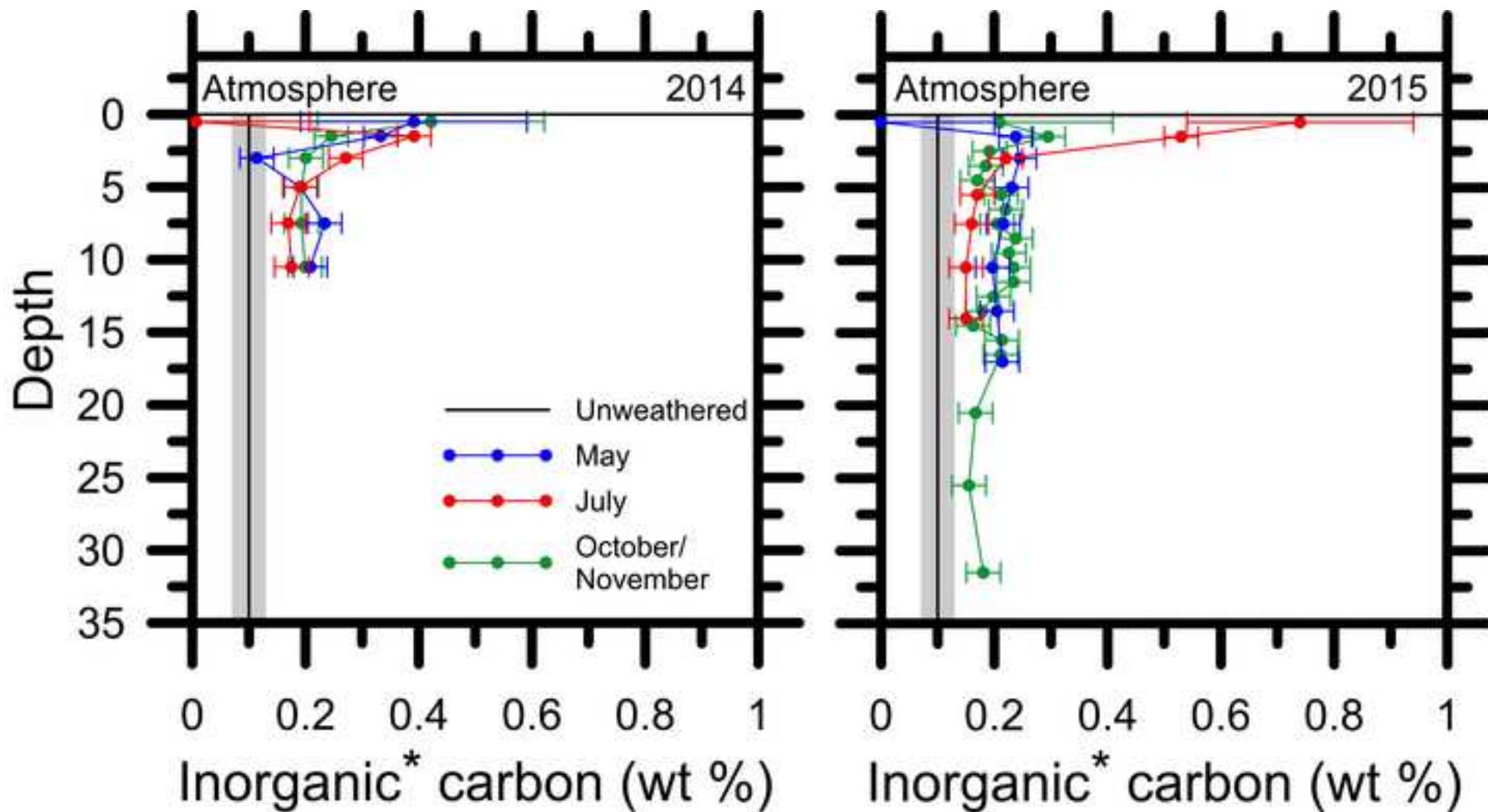


● EPMA analyses

Stoichiometric compositions :

- | | |
|--------------|--------------------------------|
| Natural | "Without" H_2O |
| ● Brucite | ▲ Nesquehonite |
| ■ Chrysotile | ▲ Dypingite |
| | ▲ Hydromagnesite |
| | ▲ Artinite |

Figure 10
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Table[Click here to download Table: Table_1.docx](#)

Month	Temperature (°C)	Solar radiation intensity (W/m ²)	Relative humidity (%)	Total precipitaions (mm)
January	-18	33	87	51
February	-17	68	82	16
March	-7	124	76	15
April	-1	178	69	51
May	10	210	69	90
June	15	231	71	64
July	17	207	79	95
August	16	164	83	103
September	12	114	87	96
October	7	70	78	115
November	-2	47	91	71
December	-11	39	91	66

Table 1: Summary of the meteorological data collected between July 2011 and September 2016.

Supplementary Interactive Plot Data (CSV)

[Click here to download Supplementary Interactive Plot Data \(CSV\): Carbon content and mineralogy.xlsx](#)

Supplementary Interactive Plot Data (CSV)

[Click here to download Supplementary Interactive Plot Data \(CSV\): Leachate water chemistry.xlsx](#)

Declaration of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.