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EXTREME WEATHERING EXPERIMENTS ON THE BURRUP PENINSULA / MURUJUGA WEATHERED GABBROS AND GRANOPHYRES

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EXECUTIVE SUMMARY

The Burrup Peninsula/Murujuga is around 30 km long and 6 km wide and is located 1300 km from Perth in Western Australia. The Peninsula is of unique cultural and archaeological significance as it contains Australia's largest and most important collection of indigenous petroglyphs. Alongside the petroglyphs, the Burrup Peninsula/Murujuga hosts several large industrial complexes including iron ore, liquefied natural gas production, salt production and fertilisers with one of Australia's largest ports. Some of the petroglyphs are close to the industrial areas and there has been public concern expressed that the petroglyphs could be damaged by airborne emissions from the industry. In 2003, the former Burrup Rock Art Technical Working Group commissioned a number of studies to monitor the petroglyphs. They included air dispersion modelling studies, air quality and microclimate, colour change, dust deposition and accelerated weathering study and mineral spectroscopy. These studies were based on the monitoring of seven sites with two control sites located on the northern Burrup Peninsula/Murujuga area and the other five located further south on the lower Burrup Peninsula/Murujuga, closer to the industrial areas. The site selection for sites close to industry and for distant "control" sites were based predominantly on predicted gas concentrations derived from modelling by SKM. In addition geology was important to ensure that both of the major rock types that supported the petroglyphs, granophyre and gabbro, were included. Between 2004 and 2013, petroglyphs at seven specially selected sites (chosen under the guidance of indigenous elders) in the Burrup Peninsula/Murujuga were measured using colour and reflectance spectroscopy measurements (the other monitoring studies have ceased in 2008). Three spots on each engraving and three spots on each background rock were measured in situ using a portable spectrophotometer for colour measurement and a reflectance spectrometer for visible and near infrared spectral analysis. In 2014, the rock art-monitoring project expanded at the request of Yara Pilbara Nitrates Pty Ltd and an additional three sites were selected. After initial monitoring in February 2014, the three new sites have become part of the monitoring program. As well as the three new sites, an extra spot (both engraving and background) was added on each monitored petroglyph panel bringing to eight sampling spots (four areas classified as 'engraving' and four areas classified as 'background') to increase the accuracy of future statistical analysis of measurements. All the results of the monitoring study have been reported in Duffy et al. (2017).

In 2016, CSIRO started an experimental extreme weathering study funded by industry through the Western Australian Department of Environment Regulation. This study aims at understanding the effect of air pollution from the industrial complexes on the petroglyphs and the surrounded weathered rocks. Samples of weathered gabbros and granophyres were collected at each of the monitoring study original seven sites (1, 2, 4, 5, 6, 7 and 8) in the Burrup Peninsula/Murujuga. One hundred and twenty six (126) rock cylinders from all original seven sites of the Burrup Monitoring program (Duffy et al., 2017) were prepared. They include fifty-five (55) gabbro samples from Site 1 (45 drilled samples) and Site 7 (10 drilled samples) and fifty-five (55) granophyre samples from Sites 2 (12 drilled samples), Site 4 (22 drilled samples), Site 5 (two (2) drilled samples), Site 6 (seven (7) drilled samples) and Site 8 (12 drilled samples). Four samples of gabbros and four samples of granophyres were subjected to a similar solution to provide more representativity. To undertake this study, a customised sample preparation was devised so only the weathered surface of the rocks (110 weathered surface and 16 fresh surface cylinders) is in contact with the solutions. The solutions included four types of pollutants comprising nitric and sulphuric acid, ammonia and ammonium nitrate. Distilled water was also used as a control. All the material (silicone, resin, vessels and solutions) used to prepare and submerged the samples were also chemically characterised to assess their potential influence on the results. All the samples were immersed in reaction vessels at 50°C with five solutions. These solutions include (1) distilled water (control); (2)nitric acid (0.00001 M pH 4.4, 0.0001 M pH 3.6, 0.001 M pH 2.8 and 0.0087M pH 2.0); (3) sulphuric acid (0.00001 M pH 4.3, 0.0001 M pH 3.4, 0.001 M pH 2.6 and 0.011M pH 1.9); (4) ammonium nitrate (0.001 M pH 4.8 and 1M pH 5.3) and (5) ammonia (0.001M pH 9.2 and 1M pH 11.5). The solutions were heated at 50°C as this temperature can be reached on the surface of the rock in summer in the Burrup Peninsula/Murujuga. This temperature also increases the kinetics of the reaction. The 3-day exposure time was considered optimum as the minimum amount of time to conduct intensive analyses on the rocks after a potential large release from an industrial plant (close to the petroglyphs of the Burrup). The 1-month exposure time was considered optimum as a follow up large analytical study. Fifty-eight (58) solutions were also measured after 1-month exposure.

The solutions used to expose the hundred and twenty-six (126) samples were chemically measured and a subset of twenty-six samples were characterised before and after exposure by optical and scanning electronic microscopies, photospectrometry and reflectance spectroscopy (the last two methods are also used during our annual monitoring of the Burrup Peninsula/Murujuga).

All the samples were immersed in reaction vessels at 50°C with the five solutions. Concentrations and pH were measured respectively after 3 days and 1 month.

For the majority of the gabbros and after 3 days at 50°C, dissolution starts either at pH 3 or below for Al, Mn and Fe or more than pH 11 for Al. Some outlier results were also observed for S1-225 and S7-206 showing some dissolution of Mn (0.07 for both) in distilled water at neutral pH (7). It is rather unexpected to see such results as it would mean that under rainwater (pH = 5.5), Mn will be dissolved in natural condition which is clearly not the case, as otherwise, Mn would not be present on the surface of the Burrup weathered rocks as they have been subjected to thousands of years of rain. The other five samples exposed in distilled water show no dissolved Mn. Another outlier is S1-43 that shows no Mn in solution at pH 3.7 after 3 days but 0.07 after a month at pH 4.9; a similar concentration found for Mn in distilled water. The last two outliers are S1-14 and S7-203 showing dissolved Mn (respectively 0.06 and 0.25) at pH 5.8. Again a much unexpected result as it would mean that under rainwater (pH = 5.5), Mn will be dissolved in natural condition which is clearly not the case as mentioned above.

For the majority of the granophyres and after 3 days at 50°C, dissolution starts at pH 3.2 and below for Al, Mn and Fe or more than pH 11 for Al. Some outlier results were also observed for S4-66 and S6-244 showing some dissolution of Mn in distilled water at neutral pH (7) up to 0.25 for S6-244. Again, as we said before it is rather unexpected that Mn would be dissolved in natural condition. The five other samples exposed to distilled water do not show Mn in solution. S8-260 and S-246 are showing dissolved Mn (respectively 0.08 and 0.05) after 1 month of exposure at pH 4.8. The two other samples exposed in similar conditions show no Mn dissolved. S8-261 also shows some Mn at pH 5.5, the three other samples subjected to similar conditions show no Mn in solution. Again a much unexpected result as it would mean that under rainwater (pH = 5.5), Mn will be dissolved in natural condition which is clearly not the case as mentioned above. The last outlier sample is S6-241, which also show some Mn at pH 6.4, again unexpected for this pH level.

This study shows that quantifying the changes before and after exposure is challenging as the variations of the methods used here, SEM with EDX, photospectrometry and reflectance spectroscopy are often larger than the changes themselves. The L, a and b colour parameters, derived from the KM photospectrometer and from the ASD spectrometer did not provide a good discrimination between the samples before and after exposure.

This is a preliminary study using novel sample preparation methods to provide a new approach to determining the effects of solutions of different compositions and concentrations on rock weathering. As a scoping tool, it was very valuable in targeting future work. This study was conducted on 110 samples and the results found here should be confirmed using a larger dataset. It was not intended to serve as an exhaustive or definitive analysis of the impacts of the chosen leach solutions on granophyre and gabbro rocks nor was it intended as an indication for permissible pollution levels.

The precautionary principle should apply here and emission capable of producing pH below 5.5 (the pH of rainwater) should be considered potentially harmful.

In the last 14 years, since the start of the monitoring of the Burrup Peninsula/Murujuga, the volume of industrial activity has increased drastically in particular for iron ore production and liquefied natural gas production and their associated consequences such as port activities, trucks, 4WD, trains and vessels as well as population increase. The two Yara plants for liquid ammonia and ammonium nitrate are also now operational. In addition, public perception and political awareness for the cultural significance of the biggest rock art site in the world has increased significantly. The combination of all these parameters requires a full review and upscale of the monitoring program undertaken in the Burrup Peninsula/Murujuga since 2004. As part of this review, it is recommended that regular measurements of the pH of the weathered surface of gabbros and granophyres in the Burrup Peninsula/Murujuga be conducted as part as a larger monitoring study with more sites and new control sites. Monitoring stations including rain water gauges should be (re) installed on the Burrup Peninsula/Murujuga to measure rainfall amount, pH concentration, cations and anions as well as wet and dry deposition flux of nitrogen and sulphur.

1. INTRODUCTION

For the last 13 years (Duffy et al., 2017), the petroglyphs at seven specially selected sites (and three additional sites since 2014) in the Burrup Peninsula/Murujuga of Western Australia were measured using colour spectrophotometry and reflectance spectroscopy. The three additional sites were measured to ensure that the construction of the Yara Pilbara Nitrates Pty Ltd Ammonium Nitrate Production Facility Project was also monitored. From 2004 to 2012, three spots on each engraving and three spots on each background rock were measured *in situ* by colour spectrophotometers (BYK and KM) and reflectance spectrometer (ASD Field Spec Pro), with a 4th engraving and background spot added in 2013. The spectral measurements were co-located with the colour measurements and acquired simultaneously. Initially, at each engraving and background spot seven spectra were acquired and averaged, with this increasing to 21 repeat measurements for the photospectrometers and 10 measurements for the reflectance spectrometer at each spot in 2005 to improve the statistical robustness of the data. The spectral variation for each spot (both engraving and background) was also assessed. The colour values were crosschecked to the colour value calculated by the ASD spectrometer. All the results of this monitoring study are published in Duffy et al. (2017).

In 2016, in response to a tender issued by the Western Australian Department of Environment Regulation (WA DER), CSIRO embarked on an experimental extreme weathering study. This study is aimed at understanding the effect of air pollution from the industrial complexes including iron ore port, liquefied natural gas, and salt production and, ammonia and ammonium nitrate plants. The study consists in (1) collecting samples of weathered gabbros and granophyres sampled at each of the original 7 sites in the Burrup Peninsula/Murujuga; (2) characterising the weathered surfaces of the samples; (3) immersing the samples in reaction vessels at 50°C with 5 solutions including distilled water (control), nitric acid, sulphuric acid, ammonium nitrate and ammonia at a range of concentrations and (4) characterising the weathered surfaces of the samples after exposure.

The main goal of this study is to assess the potential damage taking place on the surface of the samples by four types of pollutants generated from industries and close to the petroglyphs including nitric and sulphuric acid, ammonia and ammonium nitrate. This will provide an assessment of the concentrations and the associated pH from which damage can occur. It will also provide an indication of the precision of the colour and mineralogical measurements.

2. LOCATION AND SAMPLING

The rock samples required for this study were sampled at the location of the original seven sites that were selected for the Burrup Peninsula/Murujuga monitoring program (Table 1 and Figure 1) as shown in Duffy et al. (2017). These sites were initially selected by the former Burrup Rock Art Monitoring Management Committee and the final decision for a representative petroglyph at each site (each site contains one or more petroglyphs) was determined in consultation with the Committee's Technical Advisor and nominated representatives of the local indigenous communities including members of Murujuga Aboriginal Corporation.

For the record, the site selection for sites close to industry and for distant "control" sites were based predominantly on predicted gas concentrations derived from modelling by SKM (modelling is available on the WA DER website). In addition geology was important to ensure that both of the major rock types that supported the petroglyphs, granophyre and gabbro, were included.

Table 1: Details of the sites for colour and spectral mineralogy measurements (site 3 is not included in this study)

Site	Site name	Coordinates (GDA 94, Zone 50)	
1	Dolphin Island	484,975	7,738,503
2	Gidley Island	482,166	7,740,857
4	Woodside	477,398	7,721,980
5	Burrup Rd	475,959	7,719,771
6	Water Tanks	477,698	7,720,137
7	Deep Gorge	477,956	7,717,987
8	King Bay South	474,082	7,717,229

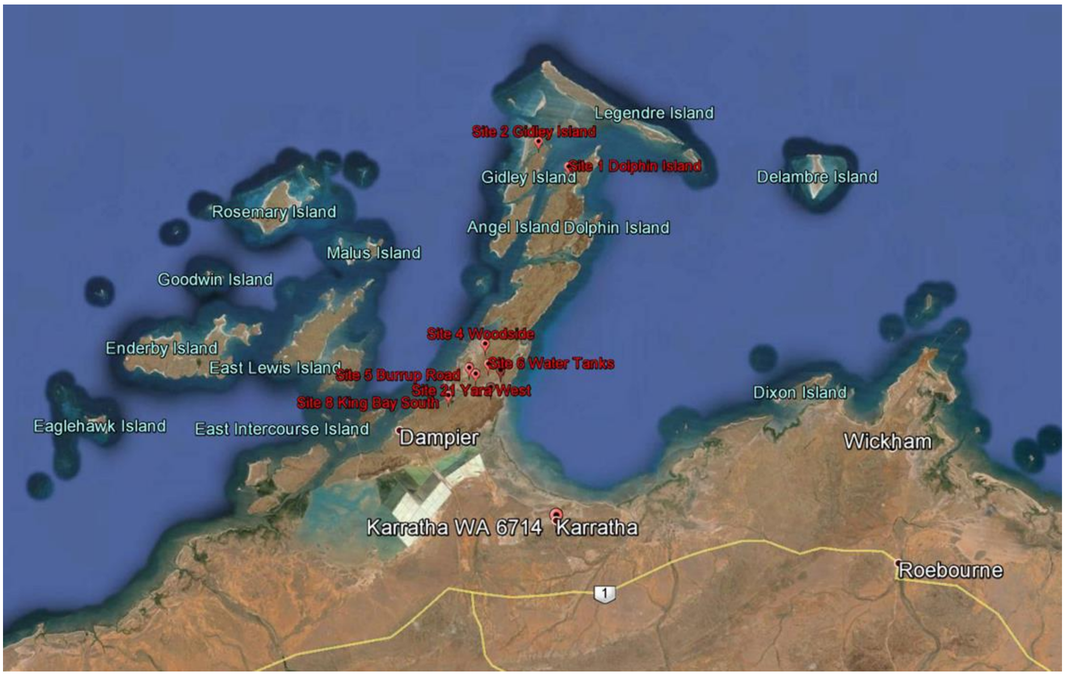


Figure 1: Google Earth® maps of the Burrup Peninsula/Murujuga with the location of the samples sites.

3. SAMPLES

From the seven sampled sites, two consist of gabbro (sites 1 and 7) and five consist of granophyre (Sites 2, 4, 5, 6 and 8). Sites 1 and 2 are located respectively in Dolphin and Gidley Islands away from the industries (12 km for Site 1 and 16 km for Site 2) whereas the remaining five sites (Sites 2, 4, 5, 6 and 8) are located closer to the industries. For each site, loose rock samples (1 or 2 depending on size) were collected. Each rock sample was chosen based on the similarity between its weathered surface and those of the surface of the backgrounds (measured with the ASD spectrometer) measured for the monitoring study (Duffy et al. 2017). All the samples collected at each site were used for this study. However, only the samples with the flattest surface were used for the extreme weathering experiment explaining why some sites are more represented than others are. Fifty-five (55) gabbro samples from Site 1 (45 drilled samples) and Site 7 (10 drilled samples) and fifty-five (55) granophyre samples from Sites 2 (12 drilled samples), Site 4 (22 drilled samples), Site 5 (two (2) drilled samples), Site 6 (seven (7) drilled samples) and Site 8 (12 drilled samples). The names of the samples are shown in Table 9 and Table 10. Four samples of gabbros and four samples of granophyres were subjected to a similar solution to provide more representativity.

In natural conditions in the Burrup Peninsula/Murujuga, solutions occurring at the surface of the weathered gabbros and granophyres will percolate through the samples down to the contact fresh-leached zones (Figure 2 and Figure 3). A similar effect will occur when the rocks are submerged in the various solutions used for the extreme weathering experiment. It is the reason why unweathered samples were also added to assess the weathering of a fresh sample. Eight drilled samples from fresh gabbros from Site 1 (2) and from Site 7 (6) as well as eight drilled samples from fresh granophyres from Site 2 (5), Site 5 (2) and Site 8 (1) were also prepared.

While not part of this study, the information provided below (text and Table 2, Table 3, Table 4, Figure 2 and Figure 3) extracted from Ramanaidou and Fonteneau (2017) has been added as it provides required background information pertinent for the characterisation of the samples. Note that the leached zone can be as wide as 1 to 1.5 cm.

The bulk chemical composition for the seven sites (Table 2) shows that fresh gabbro contains less silica (SiO_2) than fresh granophyre (52% as opposed to 70%); on the other hand, Al_2O_3, FeO, MgO, CaO and LOI are generally higher in the gabbro. In the weathered surface (Table 3), Fe_2O_3 increases for both rock types especially for granophyre where it doubles in concentration. MnO and P_2O_5 increase (Table 3). The concentrations of SiO_2, Na_2O, CaO and MgO decrease. As far as the mineralogy is concerned, both fresh gabbro and granophyre are dominated by quartz, feldspar and chlorite. Although quartz and chlorite subsist in smaller amounts in the surface coating, feldspar either, have decreased significantly or disappear totally, hematite [Fe_2O_3] and kaolinite [$Si_2Al_2O_5(OH)_4$] increase in the surface coating (Table 4).

Table 2 Bulk rock analyses of the major elements of the fresh part of the collected samples. LOI is the loss on ignition at 1000°C (From Ramanaidou and Fonteneau, 2017).

Oxides (%)	**Site1**	**Site2**	**Site4**	**Site5**	**Site6**	**Site7**	**Site8**
SiO_2	52.42	76.65	70.65	71.36	70.78	52.18	70.67
TiO_2	1.15	0.45	0.55	0.54	0.55	0.43	0.55
Al_2O_3	13.54	9.64	12.51	12.26	12.65	15.24	12.54
Fe_2O_3	2.93	1.65	2.59	2.58	1.64	1.79	2.35
FeO	7.17	2.14	2.42	2.28	3.05	5.81	2.66
MnO	0.18	0.068	0.094	0.088	0.072	0.16	0.096
MgO	6.25	1.43	0.82	0.83	1.84	7.73	1.24
CaO	10.22	0.52	1.74	2.62	0.69	11.53	1.46
Na_2O	2.05	2.98	3.95	3.36	4.25	1.82	3.88
K_2O	0.73	2.41	3.52	3.21	2.81	0.62	3.08
P_2O_5	0.07	0.13	0.15	0.14	0.14	0.03	0.15
SO_3	0.10	0.02	0.02	0.01	0.01	0.01	0.11
LOI	2.18	1.31	0.59	0.61	0.61	2.1	0.85
Total	98.99	99.41	99.59	99.89	99.10	99.45	99.64

Table 3 Chemistry comparison for each zone for Site 1 and Site 5 (FR: fresh rock and SU: surface). Fe_2O_3 (T) includes Fe^{2+} and Fe^{3+} minerals (From Ramanaidou and Fonteneau, 2017).

Oxides (%)	Site1 FR	Site1 SU	Site5 FR	Site5 SU
SiO_2	52.42	50.53	71.36	66.56
TiO_2	1.15	1.04	0.54	0.75
Al_2O_3	13.54	17.94	12.26	11.62
Fe_2O_3 (T)	10.89	12.21	5.12	10.05
MnO	0.18	0.71	0.09	0.65
MgO	6.25	2.51	0.83	0.52
CaO	10.22	5.18	2.62	0.86
Na_2O	2.05	0.55	3.36	0.62
K_2O	0.73	1.18	3.21	1.38
P_2O_5	0.07	0.84	0.14	0.81
SO_3	0.10	0.13	0.01	0.26
LOI	2.18	4.84	0.61	3.04

Total	98.99	97.66	99.89	97.12

Table 4 Relative mineralogy of (1) the fresh rocks for all sites, (2) the leached zone for Site 1 and Site 5 and (3) the surface coating for all sites obtained by XRD (bold letters for dominant minerals; normal letter for minor minerals and **italic letter for trace minerals). Quartz (Qtz); Chlorite (Chl); Illite (Ill); Amphibole (Amp); Feldspar (Fld); Augite (Aug); Actinolite (Act); Goethite (Goe); Epidote (Epi); Muscovite (mus); Stilpnomelane (Sti); Hematite (Hem); Manganese oxides (MnOx); Kaolinite (Kao); Magnetite (Mgt); Ilmenite (Ilm); maghemite (mgh) from Ramanaidou and Fonteneau (2017).**

Location Rock Type	**Mineralogy fresh rock**	**Mineralogy surface coating**
Site 1 Gabbro	**Qtz Fld Act Chl** Aug Epi Mus	**Qtz Chl** Ill Kaol *Act Fld Epi Hem Goe MnOx Aug*
Site 2 Granophyre	**Qtz Fld Chl** *Mag Hem Epi Mus*	**Qtz Chl** Fld Hem
Site 4 Granophyre	**Qtz Fld Sti** Chl Amp *Epi Mus Mag Hem*	**Qtz Fld** Kao Hem *Ill*
Site 5 Granophyre	**Qtz Fld Chl** Sti Act *Epi Mus Mag Hem*	**Qtz** Kaol *Fld Hem Mgh Epi*
Site 6 Granophyre	**Qtz Fld Chl** *Mus Mag Hem*	**Qtz** Kaol Hem Fld *Chl Mgh*
Site 7 Gabbro	**Qtz Fld Chl Act** Aug Mus Epi	**Qtz** Kaol Fld *Chl Hem Mgh*
Site 8 Granophyre	**Qtz Fld Chl** *Epi Mus Mag Hem*	**Qtz Chl** Ill Plg Kaol *Amp Aug Epi Hem Goe Ilm*

Figure 2 Top: Site 5 Weathered granophyre with (1) fresh rock, (2) leached zone and (3) surface coating. Bottom: Site 1 Weathered gabbro with (1) fresh rock, (2) leached zone and (3) surface coating. The Black Rectangle is shown in details in Figure 3.

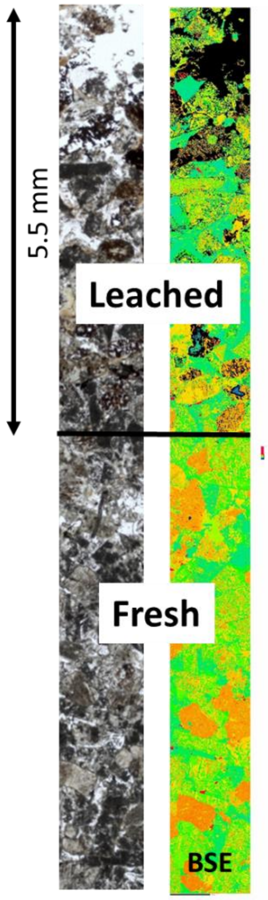


Figure 3: The microphotography in transmitted light (left) of the Black Rectangle shown in Figure 2 together with the backscattered electron or BSE (Right) image clearly show the boundary between Fresh and Leached zones as porosity increases.

4. SAMPLE PREPARATION

One hundred and twenty six (126) 10 mm diameter cylinders of rocks were drilled from all the seven sites (Figure 4). From the 126 samples (as discussed in the previous paragraph), 16 samples were fresh (no weathered surface) and 110 show a weathered surface. The surface of the rocks collected at each site varies slightly meaning that the surface coating of each rock cylinder is somewhat different from another at one particular site. It also means that rock cylinders from the same rock type (gabbro or granophyre) but from different sites will also vary. This is the result of the natural colour and mineralogical variation of each rock.

To simulate what happens naturally in the Burrup Peninsula/Murujuga, it is critical that only the weathered surface of the sample (for the weathered samples) be in contact with the solutions. This required a bespoke and precise sample preparation. An innovative and complex sequence of sample preparation was designed to ensure that only the weathered surface of the sample be in contact with the solutions as it is the case in the Burrup Peninsula/Murujuga. The sequence of sample preparation consists of seven steps (Figure 5):

(1) a cylinder of resin with a double diameter was manufactured (Figure 5, Step 1) and inserted into a silicone solution which is left to dry for 1 day to;
(2) create a silicone cast (Figure 5, Step 2);
(3) a rock cylinder (Figure 5, Step 3 right) is inserted into the silicone cast and resin poured to create a solid base (Figure 5, Step 3 left);
(4) sticky tape is glued around the rock cylinder with the resin base (Figure 5, Step 4 left) and silicone is poured on the top (Figure 5, Step 4 right) to create a protection for the surface of the rock cylinder, drying time is 1 day;
(5) when the silicone is dry, the sticky tape is removed and the 10 mm silicone protected rock cylinder is inserted into a 13 mm silicone mould. Resin is then poured around the rock cylinder where the resin coats and protects the fresh surface of the rock cylinder (Figure 5, Step 5), drying time is 1 day, when the resin is dry, the silicone protection is removed;
(6) the fresh part of the rock is now encased in resin and only the weathered surface is accessible (Figure 5, Step 6);
(7) the extra resin wall is removed by hand grinding and the sample is now ready for exposure to the solutions (Figure 5, Step 7).

As shown in Figure 2 and Figure 3, the penetration of the solution in the rock cylinders submerged in the various solutions is around 5.5mm. The diameter of the rock cylinders is 10 mm, hence the volume of the rock subjected to the solution is $(\pi \times 5^2) \times 5.5 = 432 \text{ mm}^3$; assuming a density of the rock of 2.6, each cylinder weight is around 1.123g.

Figure 4. Drilling holes after the 10 mm diameter cylinders were removed from a gabbro (Left) and a granophyre (Middle). Rock cylinder ranging from grey fresh rock to orange weathered surface (Right).

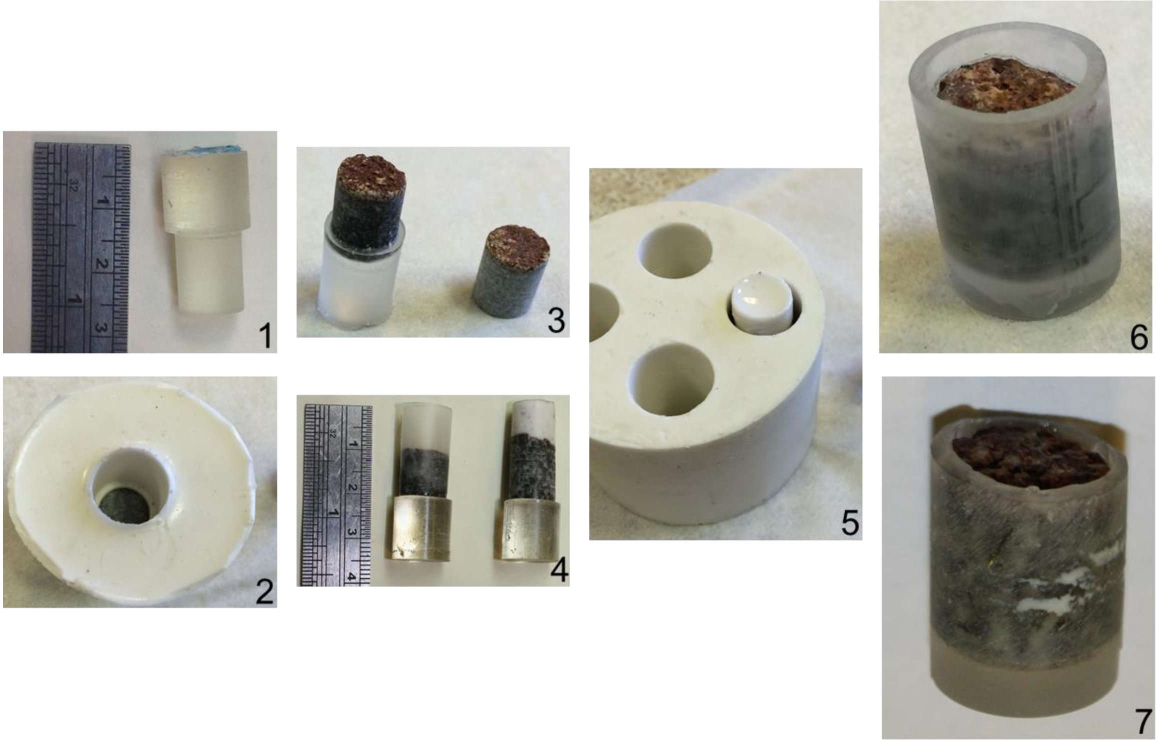


Figure 5. A cylinder of resin with a double diameter was manufactured (Step 1) and inserted into a silicone solution which is left to dry for 1 day to create a silicone cast (Step 2). A rock cylinder (Step 3 right) is inserted into the silicone cast and resin poured to create a solid base (Step 3 left). A sticky tape is glued around the rock cylinder with the resin base (Step 4 left) and silicone is poured on the top (Step 4 right) to create a protection for the surface of the rock cylinder, drying time of 1 day. When the silicone is dry, the sticky tape is removed and the 10 mm silicone protected rock cylinder is inserted into a 13 mm silicone mould. Resin is then poured around the rock cylinder where the resin coats and protects the fresh surface of the rock cylinder (Step 5), drying time is 1 day, when the resin is dry, the silicone protection is removed. The fresh part of the rock is now encased in resin and only the weathered surface is accessible (Step 6). The extra resin wall is removed by hand grinding and the sample is now ready for exposure to the solutions (Step 7).

As during sample preparation, resin and silicone were used to prepare the rock cylinders, it seemed appropriate to exposed both resin and silicone to similar conditions than the rock cylinders themselves to assess any potential interference and the results will be shown in the Chemical results section.

NOTE: This is the first time a study of this nature has been conducted and it is difficult to ensure that only the surface layer of the rock is exposed to the leach solution. This study exposed only the available surface for reaction with the leachate. Any residual silicone was washed off with double ethanol and water rinses prior to leaching and a visual confirmation was used to check that all rocks were well wetted. The samples were analysed by a scanning electron microscope and silicone was detected on the edge of the cylinder in contact with the resin and with a few residue in some holes. The cylinders were measured using the ASD spectrometer, which measures the surface of the sample. If the silicone was covering the sample, then the reflectance spectra of the minerals would have disappeared which is not the case. Finally, if the silicone was protecting the rock, we would not see a dissolution increasing with higher concentration (see Table 9 and 10) as silicon does not dissolve even a very low or very high pH (Table 6).

5. SOLUTIONS

The solutions used here simulate the pollutants potential occurring in the Burrup Peninsula/Murujuga and they include:

1) Distilled water (pH 7)
2) HNO_3
    a) 0.00001 M (pH 4.4)
    b) 0.0001 M (pH 3.6)
    c) 0.001 M (pH 2.8)
    d) 0.0087M (pH 2.0)
3) H_2SO_4
    a) 0.00001 M (pH 4.3)
    b) 0.0001 M (pH 3.4)
    c) 0.001 M (pH 2.6)
    d) 0.0111M (pH 1.9)
4) NH_4NO_3
    a) 0.001 M (pH 4.8)
    b) 1M (pH 5.3)
5) NH_3
    a) 0.001M (pH 9.2)
    b) 1M (pH 11.5)

The solutions were also heated at 50°C as this temperature can be reached on the surface of the rock in summertime in the Burrup Peninsula/Murujuga. This temperature also increases the kinetics of the reaction.

The 3-day exposure time was considered optimum as the minimum amount of time to conduct intensive analyses on the rocks after a large release from an industrial plant (close to the petroglyphs of the Burrup). The 1-month exposure time was considered optimum as a follow up large analytical study.

6. METHODS

6.1 Chemical composition measurements

The samples were analysed on simultaneous ICP-AES instruments (Vista-Pro) from Agilent Company using CSIRO approved proprietary methodology. The presented/reported variance includes all deviations coming from precision measurements, sample handling and processing as well as recoveries. Elements analysed are Fe, Mn, Al, Si, Na, and K. All the solutions have also been retained for future analyses if required.

The solutions and concentrations include distilled water (control), nitric acid or HNO_3 (0.00001 M; 0.0001 0.001 M and 0.0087 M); sulphuric acid or H_2SO_4 (0.00001 M, 0.0001 M, 0.001 M and 0.0111 M); ammonium nitrate or NH_4NO_3 (1 M and 0.001 M) and ammonia or NH_3 (1M and 0.001M). Detection limits for the elements analysed are Fe: 0.1 mg/l; Mn: 0.03 mg/l; Al: 0.1 mg/l; Si: 1 mg/l; Na: 0.2 mg/l and K: 0.1 mg/l. The rock cylinders were submerged in the plastic vessels containing 100 ml of the solutions (Figure 6).

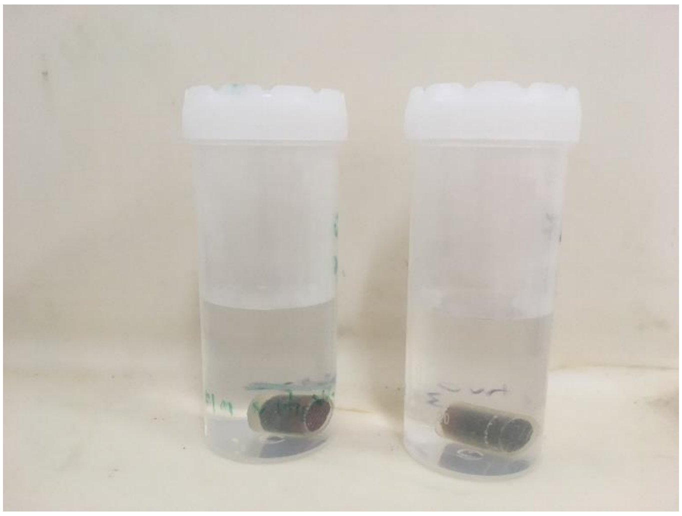


Figure 6: Rock cylinders in the solutions in their plastic vessels.

The pH meter used is a TPS WP-80D Dual pH ORP deg C model, from Rowe Scientific. The pH probes are Ionode IJ44A models. The measurement of pH is quite difficult for low concentration solution such as distilled water (or low concentration of HNO3 for instance) and the probe was left in the solution for 10 min before the measurement is completed. It is much more difficult and less accurate to measure solution with no cations (such as distilled water for instance) as there is low conductivity.

6.2 Optical Microscopy

The optical microscopy was collected using a LEICA Binocular microscope (MZ12) linked to a QImaging ROHS digital camera (Micropublisher 5.0 RTV). The digital photos were processed using QCapture Software.

6.3 Scanning Electron Microscopy

A Zeiss Ultra Plus scanning electron microscope with a Bruker e Flash detector was used to acquire Energy Dispersive Spectroscopy (EDS) maps. The condition used were 30 KV, 3 nA, an acquisition time of 2 ms per pixel with 1500 pixels an a pixel size of 5µm. Total acquisition time for a rock cylinder is 66 minutes measuring an area of 7mm (height) and 8 mm (width).

6.4 Colour Measurement

A Hand-held spectrophotometer Konica Minolta CM-700d (KM) was used to measure the samples. It measures the colour of the surface of the rock sample as a point in three-dimensional L*a*b* colour space (L* - degree of lightness, a* - degree of red/green, b* - degree of yellow/blue). The spectrophotometer has a flat conical head configuration that provided an improved repeatability on the rougher rock surfaces (Figure 7 Left). The instrument specifications are given in Table 5. Measurements were acquired using the SCI mode, where specular and diffuse reflectances are included. This type of colour evaluation measures total appearance independent of surface conditions.

The cylinders were included in the centre of the holder (Figure 7 Right) and measured 10 times after nine rotations of 40°angle of the holder.

Figure 7: Konica Minolta CM-700d spectrophotometer (Left). Measurement holder and sample in the centre (Right).

Table 5: Instrument Specifications for the Konica Minolta CM-700d spectrophotometer.

Colour Space L*a*b*	**Observer** 10^{O}	**Illuminant** D65 –simulated daylight	**Measurement/ illumination area** MAV: Φ6 mm
Light source Pulsed xenon lamp (with UV cut filter)	**Measurement time** Approx. 1 second	**Repeatability** Spectral reflectance: Standard deviation within 0.1%	

6.5 Reflectance Spectroscopy Measurement

An Analytical Spectral Device (ASD) FieldSpecPro field spectrometer was used and covers the spectral range 400-2500 nm with a spectral resolution of three nm at 700 nm using three detectors: a 512 element Si photodiode array for the 400-1000 nm range and two separate, TE cooled, graded index InGaAs photodiodes for the 1000-2500 nm range. The input is through a1.4 m fibre optic. The average scanning time to acquire a spectrum is 1 second. The ASD was operated by using an internal source of light to eliminate any external light interference. The absolute measurements are obtained using a white reference plate made of compressed polytetrafluoroethylene (PTFE), commercially available as Spectralon that reflects 100% of the light in the 380 to 2500 nm wavelength range.

A custom holder for the rock cylinder measurements by the ASD was manufactured and it consists of a spring loaded mechanism that pushes the white Spectralon cylinder and/or the rock sample into a hole in the middle of a black painted (black from 380 to 2500 nm) aluminium plate (Figure 8). The dimension of the central hole has been calculated so the resin surrounding the rock cylinder does not show during measurements. A custom resin cylinder with the internal diameter identical to the head of the probe was constructed, centred, and screwed on the top of the black aluminium plate to ensure that the head of the probe is always at the same location. As for the colour measurements, the rock cylinders were measured ten times after nine rotations of the probe (40°angle) (Figure 9).

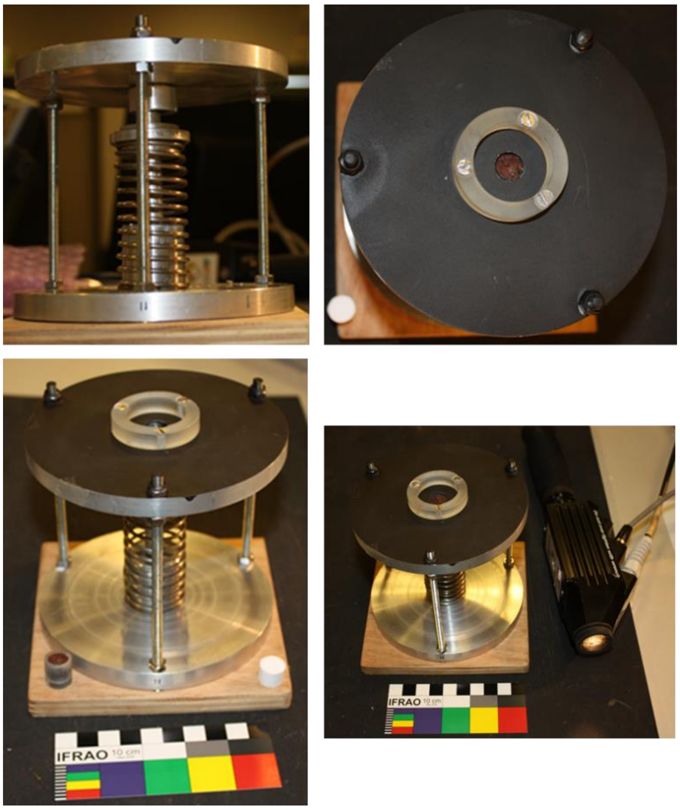


Figure 8. A custom holder for the rock cylinder measurements by the ASD was manufactured (Top Left). It consists of a spring loaded mechanism that pushes the white Spectralon cylinder and/or the rock sample into a hole in the middle of a black painted (black from 380 to 2500 nm) aluminium plate (Top Right). The dimension of the central hole has been calculated so the resin surrounding the rock cylinder does not show during measurements (Top Right). A custom resin cylinder with the internal diameter identical to the head of the probe was constructed, centred and screwed on the top of the black aluminium plate to ensure that the head of the probe is always at the same location.

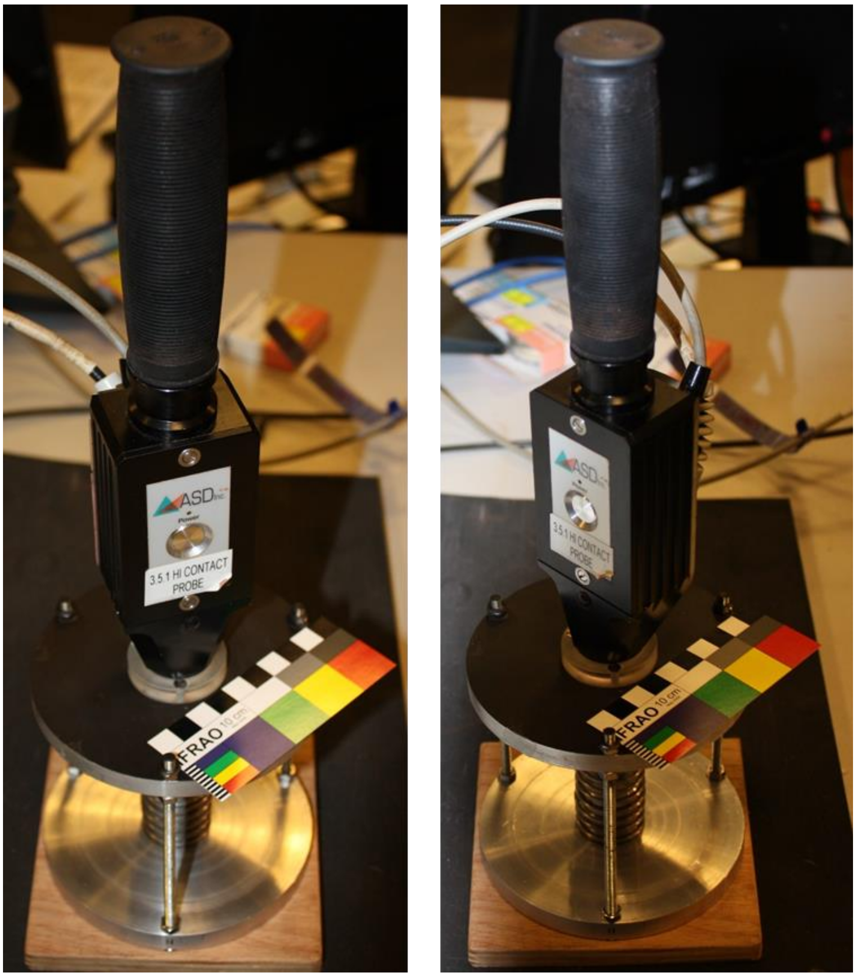
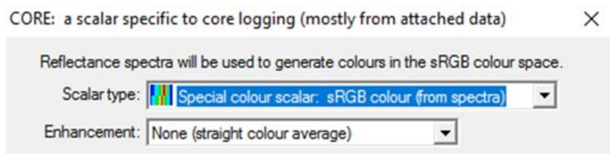


Figure 9. The rock cylinders were measured 10 times after nine rotations of the probe (40°angle).

The ASD spectra were imported into the CSIRO-developed The Spectral Geologist or TSG™. The raw ASD spectra were converted into absolute reflectance. For each of the 10 spectra, six parameters were extracted and they include:

1. L*a*b* colour space (L* - degree of lightness, a* - degree of red/green, b* - degree of yellow/blue);
2. Depth of the 900 nm iron oxide absorption (D900nm)
3. Minimum wavelength of 900 nm iron oxide absorption (MinW900nm)
4. Depth of the Chlorite 2350 nm absorption (DChl)
5. Depth of the Kaolinite 2206 nm absorption (DKaol)
6. Depth of the Gibbsite 2257 nm absorption (DGib)

All the calculations required to measure these parameters are shown in Figure 10.



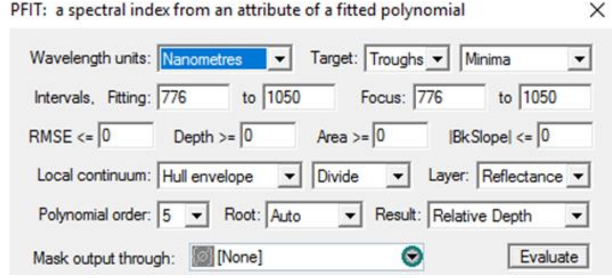
CORE: a scalar specific to core logging (mostly from attached data)

Reflectance spectra will be used to generate colours in the sRGB colour space.

Scalar type: Special colour scalar: sRGB colour (from spectra)

Enhancement: None (straight colour average)

L a b calculation in TSG



PFIT: a spectral index from an attribute of a fitted polynomial

Wavelength units: Nanometres Target: Troughs Minima

Intervals, Fitting: 776 to 1050 Focus: 776 to 1050

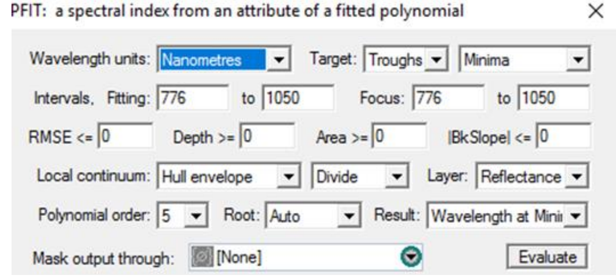
RMSE <= 0 Depth >= 0 Area >= 0 |BkSlope| <= 0

Local continuum: Hull envelope Divide Layer: Reflectance

Polynomial order: 5 Root: Auto Result: Relative Depth

Mask output through: [None]

Depth of the 900 nm iron oxide absorption (D900nm) calculation in TSG



PFIT: a spectral index from an attribute of a fitted polynomial

Wavelength units: Nanometres Target: Troughs Minima

Intervals, Fitting: 776 to 1050 Focus: 776 to 1050

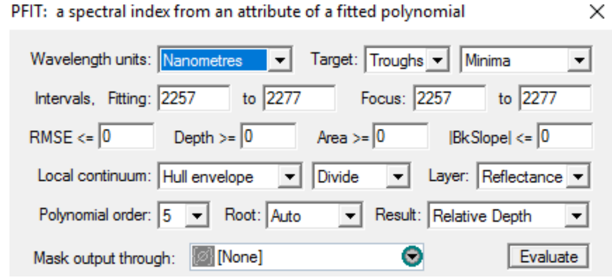
RMSE <= 0 Depth >= 0 Area >= 0 |BkSlope| <= 0

Local continuum: Hull envelope Divide Layer: Reflectance

Polynomial order: 5 Root: Auto Result: Wavelength at Mini

Mask output through: [None]

Minimum Wavelength of the 900 nm iron oxide absorption (D900nm) calculation in TSG



PFIT: a spectral index from an attribute of a fitted polynomial

Wavelength units: Nanometres Target: Troughs Minima

Intervals, Fitting: 2257 to 2277 Focus: 2257 to 2277

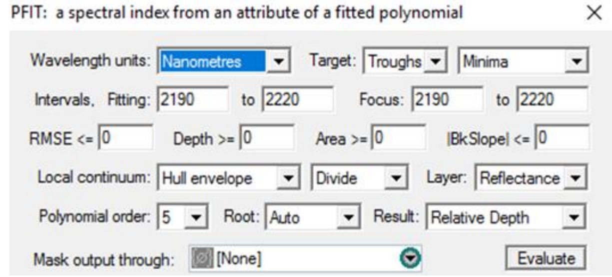
RMSE <= 0 Depth >= 0 Area >= 0 |BkSlope| <= 0

Local continuum: Hull envelope Divide Layer: Reflectance

Polynomial order: 5 Root: Auto Result: Relative Depth

Mask output through: [None]

Depth of the Chlorite 2350 nm absorption (DChl) calculation in TSG



PFIT: a spectral index from an attribute of a fitted polynomial

Wavelength units: Nanometres Target: Troughs Minima

Intervals, Fitting: 2190 to 2220 Focus: 2190 to 2220

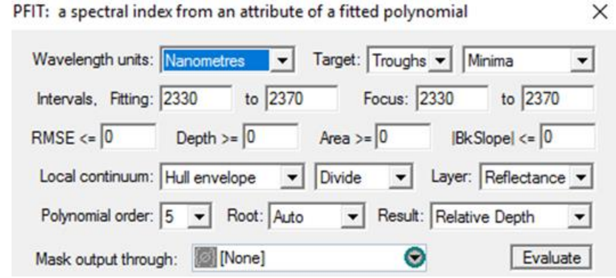
RMSE <= 0 Depth >= 0 Area >= 0 |BkSlope| <= 0

Local continuum: Hull envelope Divide Layer: Reflectance

Polynomial order: 5 Root: Auto Result: Relative Depth

Mask output through: [None]

Depth of the Kaolinite 2206 nm absorption (DKaol) calculation in TSG



PFIT: a spectral index from an attribute of a fitted polynomial

Wavelength units: Nanometres Target: Troughs Minima

Intervals, Fitting: 2330 to 2370 Focus: 2330 to 2370

RMSE <= 0 Depth >= 0 Area >= 0 |BkSlope| <= 0

Local continuum: Hull envelope Divide Layer: Reflectance

Polynomial order: 5 Root: Auto Result: Relative Depth

Mask output through: [None]

Depth of the Gibbsite 2257 nm absorption (DGib) calculation in TSG

Figure 10: Calculation details of the 6 parameters calculated from each spectrum in TSG.

6.6 Statistical analysis

Both the KM and ASD data were statistically analysed to assess if there was a significant difference between and after the various chemical exposures. A t-Test with two-sample assuming equal variances was used. For this study, we used P (T<=t) two-tail as the best way of assessing a potential difference between and after exposure. If P (T<=t) two-tail is less than 0.05 then there is a significant difference and if it is more than 0.05 there is no significant difference.

7. RESULTS AND DISCUSSION

7.1 Chemical results

7.1.1 MATERIAL USED FOR SAMPLE PREPARATION AND SOLUTIONS

The five resin and five silicone samples used to prepare the rock cylinders were exposed to distilled water and the higher concentrated solutions (Table 6). Apart for the silicone in water, the pH of all the other solutions remains constant from 4 hours to 3 days. The pH of solution of the silicone in distilled water is basic (pH 8) after 4 hours and decrease to a pH of six after 1 day and remain constant throughout the experiment. The silicone and the resin can potentially add up to 0.1 mg/l of Fe, 0.1 mg/l of Al, 5 mg/l of Si, 1.9 mg/l of Na and 0.2 mg/l of K to the results (Table 6). The water used for the control experiment, the bottle rinse (each sample was exposed to the various solutions in a vessel and a bottle rinse using distilled water was also carried out), the 1M NH_4NO_3, 0.0087M HNO_3, 0.0111M H_2SO_4 and the 1M NH_3 solutions were also measured to assess potential source of contamination (Table 7). Apart from water that can bring up to 4mg/l of Si and 1.8 mg/l of Na, all the other solutions are very clean. It should be noted that even under extreme conditions (0.0087 M HNO_3, 0.0111M H_2SO_4, 1 M NH_4NO_3 and 1M NH_3) the silicone is not dissolved.

Table 6: pH and chemical composition of Silicone and resin in the stronger exposure solutions (in bold, positive values)

Name	**Solutions**	**pH**				**3 Days (mg/l)**					
		4 hr	**1 day**	**2 days**	**3 days**	**Fe**	**Mn**	**Al**	**Si**	**Na**	**K**
silicone 1	H_2O	7.9	5.8	5.9	6.0	0.0	0.00	**0.1**	0	**0.1**	0.0
silicone 2	0.0087 M HNO_3	2.2	2.2	2.0	2.1	0.0	0.00	**0.1**	0	**0.1**	0.0
silicone 3	0.0111 M H_2SO_4	2.0	1.9	1.8	1.9	0.0	0.00	0.0	0	0.0	0.0
silicone 4	1 M NH_4NO_3	11.5	11.4	11.4	11.5	0.0	0.00	0.0	**4**	**1.8**	**0.1**
silicone 5	1M NH_3	4.9	4.8	4.8	5.0	0.0	0.00	0.0	0	**0.1**	0.0
resin 1	0.01 M HNO_3	2.2	2.1	2.0	2.0	0.0	0.00	0.0	**1**	**0.2**	0.0
resin 2	0.01 M H_2SO_4	2.2	1.9	1.9	1.9	**0.1**	0.00	**0.1**	**1**	**0.1**	**0.1**
resin 3	1 M NH_4NO_3	11.4	11.4	11.4	11.5	0.0	0.00	0.0	**1**	**0.1**	0.0
resin 4	1M NH_3	5.5	5.7	5.8	6.1	0.0	0.00	**0.1**	**5**	**1.9**	**0.2**
resin 5	H_2O	6.31	7.63	7.15	6.37	0.0	0.00	0.0	0	**0.0**	**0.1**

Table 7: chemical composition of water used for the control experiment, the bottle rinse, the 1M NH_4NO_3, 0.0087M HNO_3, 0.0111M H_2SO_4 and the 1M NH_3 solutions. In bold positive values

Name	3 Days (mg/l)					
	Fe	**Mn**	**Al**	**Si**	**Na**	**K**
50 ml bottle rinse	0.0	0.00	0.0	0	0.0	0.0
1 M NH_4NO_3 new blank	0.0	0.00	0.0	0	0.0	0.0
0.01 M HNO_3 blank	0.0	0.00	0.0	0	0.0	0.0
0.01 M H_2SO_4 blank	0.0	0.00	0.0	0	0.0	0.0
1M NH_3 blank	0.0	0.00	0.0	0	0.0	0.0
H_2O blank	0.0	0.00	0.0	**4**	**1.8**	0.0

7.1.2 FRESH ROCK CYLINDERS

The solutions from16 rock cylinders from the fresh gabbros and granophyres were also measured (Table 8). The pH measured from 4 hours to 3 days is relatively constant. The concentration of Fe, Mn and Al is nil except for S7-127 that shows 0.08 mg/l of Mn. For Si, there is an anomalous value of 108 mg/l for S2-94.

7.1.3 WEATHERED ROCK CYLINDERS

The eight different solutions used during the exposition of the one hundred and ten (110) rock cylinders from four weathered samples of gabbro and four weathered samples of granophyres were analysed (Table 9 and Table 10). The pH and the chemical composition of the solutions for the gabbros and the granophyres after 3 days and 1-month exposure at 50°C were recorded for all samples, for a subset, the pH was also recorded before the sample was in the solution (initial), after 4 hours, after 1 day or after 2 days. Four samples of gabbros and four samples of granophyres were subjected to a similar solution to provide more representativity. However, note that because of natural variability, samples from the same rock will not be identical. In Table 9 and Table 10, the orange highlights show values that are improper, that is the 1-month exposure is less than the 3 days exposure. In these cases, the 1-month exposure values are accepted as correct. The red highlights show values that are significantly positive, indicating that some dissolution of the sample has occurred.

Table 8: chemical composition of 8 fresh granophyres (S2, S5 and S8) and 8 fresh gabbros (S1 and S7). The significant values are shown in bold. Note that the 106mg/l of Si in S2-94 Fresh seems anomalous.

Name	**Solutions**	**pH**				**3 Days (mg/l)**					
		4 hr	**1 day**	**2 days**	**3 days**	**Fe**	**Mn**	**Al**	**Si**	**Na**	**K**
S7-139 Fresh	0.0001 M HNO_3	3.3	2.9	3.0	3.1	0.0	0.00	0.0	0	0.0	0.0
S7-127 Fresh	0.0001 M H_2SO_4	2.8	2.8	2.8	3.0	0.0	**0.08**	0.0	0	0.0	0.0
S7-125 Fresh	H_2O	7.2	6.6	7.9	6.3	0.0	0.00	0.0	0	0.0	0.0
S7-129 Fresh	1M NH_3	11.6	11.6	11.6	11.6	0.0	0.00	0.0	0	0.0	**0.6**
S7-33 Fresh	1 M NH_4NO_3	5.1	5.2	5.5	5.6	0.0	0.00	0.0	0	0.0	0.0
S2-98 Fresh	0.0001 M HNO_3	3.0	2.9	3.0	3.2	0.0	0.00	0.0	0	0.4	**0.1**
S2-89 Fresh	0.0001 M	2.9	2.7	2.7	2.7	0.0	0.00	0.0	**3**	0.0	0.0
S2-86 Fresh	H2O	7.7	5.6	6.7	6.7	0.0	0.00	0.0	**6**	0.0	0.0
S2-102 Fresh	1M NH_3	11.6	11.6	11.6	11.7	0.0	0.00	0.0	**1**	0.0	0.0
S2-94 Fresh	1 M NH_4NO_3	5.5	5.2	5.3	5.8	0.0	0.00	0.0	**106**	**0.2**	0.0
S8-257 Fresh	0.001 M	6.2	6.1	6.5	6.6	0.0	0.00	0.0	**5**	**1.2**	0.0
S5-113 Fresh	0.001 M HNO_3	4.1	4.1	4.2	4.4	0.0	0.00	0.0	**1**	0.0	0.0
S5-115 Fresh	0.001 M HNO_3	4.1	4.2	4.2	4.3	0.0	0.00	0.0	0	0.0	0.0
S1-20 Fresh	1 M NH_4NO_3	5.0	5.2	5.2	5.7	0.0	0.00	0.0	**11**	**0.3**	**0.1**
S7-201 Fresh	0.0001 M	7.0	5.5	6.2	6.6	0.0	0.00	0.0	0	0.0	0.0
S1-3 Fresh	0.0001 M	5.4	5.1	5.2	6.2	0.0	0.00	0.0	0	0.0	0.0

The measurement of pH is quite difficult for low concentration solution such as distilled water. It is much more difficult and less accurate to measure solution with no cations (such as distilled water for instance) as there is low conductivity, hence the variability of pH for distilled water in Table 9 (S4-79, S4-232, S2-93, S4-66, S6-244, S8-262 and S4-69 for granophyres) and Table 10 (S1-31, S1-225, S7-206, S1-6, S1-36, S1-7 and S1-29). With higher concentration of cations in solution, the pH accuracy increases and the pH values are more consistent (see Table 9, S1-47, S1-17, S1-25 and S1-16).

Gabbros

In gabbros, for distilled H_2O, Mn was measured in solution after 1 month in two out of five samples. For concentrations of 0.00001 M HNO_3, 0.0001 M HNO_3, 0.001 M HNO_3, no dissolution was observed after 3 days. For 1-month exposure, 2 out of 4 samples (S1-21 and S1-26) show some Mn in solution respectively 0.06 and 0.03 with a concentration of 0.001 M HNO_3. However even in water, Mn can be dissolved (see S1-225 and S7-226). Al is found in solution for one sample out of four for a concentration of 0.001 M HNO_3. For a concentration of 0.00087 M HNO_3 (pH = 2.3), 3 out of 4 samples show a dissolution of Mn and Al after 3 days and it is increasing after 1-month (pH = 2.2-4.0). Note that Fe was not dissolved.

In solutions of distilled H_2O and for concentrations of 0.00001 M H_2SO_4 and 0.0001 M H_2SO_4, no dissolution was observed after 3 days or 1-month exposure. For concentration of 0.001 M H_2SO_4 (pH = 2.8) and 3 days, two out of four samples show a dissolution of Mn and Al but no Fe even after 1-month. For concentration of 0.0111 M H_2SO_4 (pH 1.8 to 2.1), Fe, Mn and Al are in solution after 3 days and of course 1-month.

For concentration of 1 M NH_4NO_3 (pH 5.5 to 5.8), one sample shows Mn in solution after 3 days and confirmed after 1-month, whereas the other 3 samples are intact. A similar situation occurs for 0.001 M NH_4NO_3 (pH 6.4 to 8.5). For concentration of 1 M NH_3 (pH 7.1 to 11.7), two sample shows Al in solution after 3 days, whereas the other two samples are intact. For concentration of 0.001 M NH_3 (pH 8.3 to 9.1), no dissolution was noted.

Note that S7-207 (white letter) is clearly an outlier with such a concentration the pH should be around >11 (as shown in all other samples)

Granophyres

For distilled H_2O (pH= 6.9), Mn was measured in solution after 3days for 1 sample (0.07) out of 7 and after 1 month in two out of five samples (respectively 0.03 and 0.25). For concentrations of 0.00001 M HNO_3, one sample out of four shows Mn in solution (0.11) confirmed after 1month (0.22). For concentrations of 0.0001 M HNO_3, two sample out of four shows Mn in solution (respectively 0.05 and 0.06) confirmed after 1-month (0.1 and 0.15). For concentrations of 0.001 M HNO_3 (pH 3.0 to 3.2), three sample out of four shows Mn in solution confirmed after 1-month. For a concentration of 0.00087 M HNO_3 (pH = 2.3), two out of four show Fe in solution, all four samples show a dissolution of Mn and three out of four show Al in solution after 3 days and it is increasing after 1-month (pH = 2.2-2.3). For distilled

For concentrations of 0.00001 M H_2SO_4 and 0.0001 M H_2SO_4, no dissolution was observed after 3 days. After 1-month exposure, some samples show Mn dissolution. For concentration of 0.001 M H_2SO_4 (pH = 2.8) and 3 days, two out of four samples show a dissolution of Mn and Al and one dissolution of Fe after 1-month. For concentration of 0.0111 M H_2SO_4 (pH 1.8 to 2.0), Fe, Mn and Al are in solution after 3 days and of course 1-month. For concentration of 1 M NH_4NO_3 (pH 5.3 to 5.8), one sample shows Mn in solution after 3 days and confirmed after 1-month, whereas the other three samples are intact. A similar situation occurs for 0.001 M NH_4NO_3 (pH 5.7 to 6.1). For concentration of 1 M NH_3 (pH 11.5 to 11.8), three sample shows Al in solution after 3 days, confirmed after 1-month. For concentration of 0.001 M NH_3 (pH 8.2 to 8.4), no dissolution was noted.

Scatterplots of the chemical composition of the solutions as a function of pH are shown for the gabbros (1) for Fe. Mn and Al after 3 days of exposure (Figure 11), (2) after 1 month of exposure (Figure 12) and (3) for Si, Na and K after 1 month of exposure (Figure 13). Similar scatterplots for the chemical composition of the solutions as a function pf pH are shown for the granophyres (1) for Fe. Mn and Al after 3 days of exposure (Figure 14), (2) after 1 month of exposure (Figure 15) and (3) for Si, Na and K after 1 month of exposure (Figure 13). For the gabbros and after 3 days at 50°C, dissolution starts either at pH 3 or below for Al, Mn and Fe or more than pH 11 for Al. For the granophyres, dissolution starts at pH 3.2 and below for Al, Mn and Fe or more than pH 11 for Al. After 1 month, the pH of the solution has increased because of the dissolution for both the gabbros and granophyres. The initial pH at 3 days is the critical pH and will be used as the pH from which dissolution start to occur.

Table 9 pH and Chemical composition of the solutions for the gabbros after 3 days and 1-month exposure at 50°C. In orange values that are incorrect, that is the 1-month exposure is less than the 3 days exposure. In these cases, the 1-month exposure values are accepted as correct. The significant values are shown in red showing that dissolution of the sample has occurred. Note that S7-207 (white letter) is clearly an outlier with such a concentration the pH should be around >11 (as shown in all other samples).

Name	Solutions	pH						3 Days (mg/l)						1 Month (mg/l)					
		Initial	4 h	1 day	2 days	3 days	1 month	Fe	Mn	Al	Si	Na	K	Fe	Mn	Al	Si	Na	K
S1-31	H2O	8.2				6		0	0	0	1	0.4	0.2						
s1 225	H2O	6.3		6.2	7.5	5.9	6.7	0	0	0	0	1.9	0.4	0	0.07	0	1	5.5	0.8
s7 206	H2O			6.7	7.6	7.3	7.3	0	0	0	4	0	0.1	0	0.07	0	4	0.3	0.2
s1 6	H2O			6.7	7.6	7.4	6.4	0	0	0	2	0.4	0.2	0	0	0	4	0.6	0.3
s1 36	H2O			7.4	7.2	6.1	4.5	0	0	0	1	0.6	0.2	0	0	0	2	0.9	0.3
s1-7	H2O			6.4	7.8	7.7	7.6	0	0	0	2	0.4	0.2	0	0	0	3	0.6	0.3
s1 29	H2O	6.3	5.6	6.8	5.9	6.2		0	0	0	0	0.3	0.1						
S1-54	0.00001 M HNO3	4.4				5.6		0	0	0	0	0.5	0.1						
s1 224	0.00001 M HNO3	4.9		5.9	7.4	6.1	7	0	0	0	1	9.4	0.9	0	0	0	0	8.3	0.8
s1 15	0.00001 M HNO3			5.4	7.6	7.4	6.6	1	0	2.6	2	8.2	0.4	0	0	0	3	0.9	0.3
s1 33	0.00001 M HNO3	4.9	5.1	5.9	5.7	5.4		0	0	0	0	0	0						
s1 24	0.0001 M HNO3	4	4	4.2	4.2	4.2		0	0	0	0	0	0						
s1 12	0.0001 M HNO3			3.7	5.2	4.4	5.7	0.5	0	1.2	2	3.9	0.3	0	0	0	2	0.8	0.4
s1 39	0.0001 M HNO3	4		3.9	4.4	4.4	5.4	0	0	0	2	0.4	0.2	0	0	0	2	1	0.3
S1-38	0.0001 M HNO3	3.6				4.2		0	0.04	0	2	0.6	0.2						
S1-23	0.001 M HNO3	2.8				3.1		0	0	0	1	0.4	0.2						
s1 26	0.001 M HNO3	3		3	3.2	3.2	3.2	0	0	0	2	1.2	0.5	0	0.03	0.3	3	1.9	0.5
s1 21	0.001 M HNO3			2.9	3.2	3.1	3.3	0	0	0	3	0.4	0.4	0	0.06	0	3	0.5	0.4
s1 83	0.001 M HNO3	3	3	3	2.9	3		0	0	0	0	0.3	0.1						
s1 47	0.01 M HNO3	2.1	2.2	2.1	2	2.1		0	0	0	0	0.3	0.2						
s1 17	0.01 M HNO3			2	2.3	2.3	4	0.3	0.07	0.5	4	1.9	0.2	0	0.15	0.5	3	0.6	0.4
s1 25	0.01 M HNO3	2.1		2	2.1	2.2	2.2	0	0.08	0.2	1	1.2	1.5	0.3	0.48	1.9	2	1.2	1.7
S1-16	0.01 M HNO3	2				2.2		0	0.06	0.1	0	0.5	0.2						
S1-8	0.00001 M H2SO4	4.3				5.8		0	0	0	0	0.4	0.1						
s1 41	0.00001 M H2SO4	4.6		4.4	6.5	5.4	6.3	0.4	0	1.1	2	3.8	0.3	0	0	0	3	1.5	0.3
s1 32	0.00001 M H2SO4			4.8	5.7	6.5	6.3	0	0	0	2	0.9	0.2	0	0	0	2	1.1	0.2
s1 2	0.00001 M H2SO4	4.6	4.7	5.2	5.3	5.3		0	0	0	0	0.7	0.2						

s1 34	0.0001 M H2SO4	3.6	3.6	3.7	3.6	3.7		0	0	0	1	1	0.3						
s1 51	0.0001 M H2SO4			3.5	6.2	5.8	6.3	0	0	0	2	0.6	0.2	0	0	0	2	1.1	0.2
s1 43	0.0001 M H2SO4	3.6		3.4	3.8	3.7	4.9	0	0	0	1	1.1	1.6	0	0.07	0	2	0.9	1.6
S7-130	0.0001 M H2SO4	3.4				3.7		0	0	0	0	0.7	0.2						
S1-44	0.001 M H2SO4	2.6				2.8		0	0.03	0.1	1	0.5	0.3						
s7 209	0.001 M H2SO4			2.6	2.8	2.8	3.1	0.2	0.87	0.6	3	1.1	0.2	0	1.78	0.5	4	0.4	0.2
s1 10	0.001 M H2SO4	2.7	2.7	2.7	2.5	2.7		0	0	0.2	1	0.3	0.2						
s1 223	0.001 M H2SO4	2.7		2.9	3.3	3.7	6.2	0	0	0	1	9.6	1.2	0	0.03	0	1	7.6	0.9
s1 221	0.01 M H2SO4	1.8		1.8	1.9	2.1	3.7	0.6	0.56	2	3	9.6	1.4	0.6	1.04	2.8	3	7.4	1.2
s1 35	0.01 M H2SO4	1.8	2	1.9	1.8	2		0.5	0.08	0.6	2	0.6	0.3						
s7 204	0.01 M H2SO4			1.8	1.9	1.8	2.2	1.4	1.78	3.7	5	1.3	0.3	5	4.52	14.5	11	0.5	0.5
S1-22	0.01 M H2SO4	1.9				1.9		1.1	0.08	1	2	0.4	0.5						
S1-55	1 M NH4NO3	4.8				5.8		0	0	0	0	0.3	0.2						
s1 14	1 M NH4NO3	4.7		5	5.5	5.5	5.8	0	0	0	0	0.8	0.7	0	0.06	0	1	1.1	0.8
s7 203	1 M NH4NO3			5.1	5.6	5.8	6.1	0.1	0.25	0.4	2	1.7	0.5	0	0.42	0	2	0.6	0.6
s1 28	1 M NH4NO3	4.7	4.9	5.4	5.5	5.8		0	0	0	0	0.3	0.2						
s1 9	0.001 M NH4NO3	5.5	5.7	5.9	6	6		0	0	0	0	0.3	0.2						
s7 202	0.001 M NH4NO3			6	6.9	8.5	6.5	0	0.04	0	3	0	0.7	0	0.08	0	3	0.3	0.2
s1 1	0.001 M NH4NO3	5.5		6	6.8	6.6	6.7	0	0	0.4	1	0	0.3	0	0	0	2	1.2	0.3
S1-30	0.001 M NH4NO3	5.3				6.4		0	0	0	1	0.9	0.4						
S1-45	1M NH3	11.5				11.5		0	0	0.1	4	0.5	0.2						
s1 222	1M NH3	11.7		11.4	11.7	11.7	11.6	0	0	2.4	4	10.5	1.1	0	0	8.7	2	9.5	1.4
s7 126	1M NH3	11.7	11.6	11.6	11.5	11.6		0	0	0.2	6	0.3	0.7						
s7 207	1M NH3			11.2	11.8	**7.1**	11.6	0.1	0	0.8	16	4	0.8	0	0	1.5	16	0.4	0.4
s7 205	0.001M NH3			9.1	9	8.3	8.3	0.1	0	0.5	3	0	0.3	0	0	0	4	0.3	0.2
s7135	0.001M NH3	9.9	9.3	9.4	9.2	9.1		0	0	0	0	0.5	0.2						
S1-37	0.001M NH3	9.2				8.7		0	0	0	1	0.9	0.2						
s1 13	0.001M NH3	9.9		9.1	8.4	8.4	7.5	0.2	0	0.8	1	0	0.4	0	0	0	2	1	0.4

Table 10 pH and Chemical composition of the solutions for the granophyres after 3 days and 1-month exposure at 50°C. In orange values that are incorrect, that is the 1-month exposure is less than the 3 days exposure. In these cases, the 1-month exposure values are accepted as correct. The significant values are shown in red showing that dissolution of the sample has occurred.

Name	Solutions	pH						3 Days (mg/l)						1 Month (mg/l)					
		Initial	4 h	1 day	2 days	3 days	1 month	Fe	Mn	Al	Si	Na	K	Fe	Mn	Al	Si	Na	K
S4-79	H2O	8.2				6.8		0.0	0	0	0	0.6	0.2						
s4 232	H2O			6.7	7.5	7.1	7	0.0	0	0	0	0.3	0.4	0	0	0.0	0	0.5	0.5
s2 93	H2O			7.3	7.6	7.4	7.3	0.0	0	0	1	0.6	0.2	0	0	0.0	2	0.9	0.1
s4 66	H2O			6.5	7.4	7.2	7	0.0	0	0	4	0.3	0.2	0	0.03	0.0	4	0.5	0.2
s6 244	H2O			6.3	7	6.9	7.3	0.0	0.07	0	0	0	0.1	0	0.25	0.0	0	0.4	0.1
s8-262	H2O						7.3	0.0	0	0	0	0.3	0.1	0	0	0.0	0	0.5	0.0
s4 69	H2O	6.3	8.4	7.1	7.2	6.9		0.0	0	0	0	0.3	0						
S4-61	0.00001 M HNO3	4.4				6.7		0.0	0	0	1	0	0.1						
s4 238	0.00001 M HNO3			5.9	7.5	7.1	7.1	0.0	0	0	0	0.3	0.3	0	0	0.0	0	0.4	0.5
s6 243	0.00001 M HNO3			5.7	6.9	7.1	6.9	0.0	0.11	0	0	0.2	0	0	0.22	0.0	0	0.3	0.0
s2 96	0.00001 M HNO3	4.9	7.6	6.8	6.6	6.1		0.0	0	0	0	0.5	0.1						
s2 83	0.0001 M HNO3	4	4.1	4.1	4.1	4.2		0.0	0	0	1	0	0						
s8 260	0.0001 M HNO3			3.6	4.4	4.6	5.3	0.0	0.05	0	0	0.3	0.2	0	0.12	0.0	0	0.5	0.1
s4 236	0.0001 M HNO3			4	7.3	4.5	6.4	0.0	0.06	0	0	0.2	0.3	0	0.15	0.0	0	0.5	0.5
S2-84	0.0001 M HNO3	3.6				4.1		0.0	0	0	0	0.6	0.2						
S2-81	0.001 M HNO3	2.8				3		0.0	0	0	0	1	0.2						
s4 237	0.001 M HNO3			2.9	3.3	3.2	4.3	0.0	0.06	0	0	0.2	0.4	0	0.12	0.0	0	0.4	0.7
s8 259	0.001 M HNO3			2.9	3.2	3.2	3.4	0.0	0.13	0	0	0.4	0.2	0	0.54	0.0	0	0.6	0.2
s4 80	0.001 M HNO3	3	3.1	2.9	3	3		0.0	0.04	0	0	0.4	0.3						
s4 62	0.01 M HNO3	2.1	2.2	2.1	2	2.1		0.0	0.03	0.1	1	0	0.2						
s8 251	0.01 M HNO3			2	2.2	2.1	2.2	0.1	0.1	0.2	0	0.3	0.2	0.4	0.33	1.4	0	0.5	0.4
s4 231	0.01 M HNO3			2	2.1	2.1	2.3	0.1	1.44	1.1	0	0.3	0.6	0.6	3.16	4.1	2	0.6	1.2
S5-111	0.01 M HNO3	2				2.2		0.0	0.03	0	1	0.2	0.2						
S5-105	0.00001 M H2SO4	4.3				4.8		0.0	0	0	1	0	0						
s4 233	0.00001 M H2SO4			4.9	6.2	5.9	6.2	0.2	0	0.5	0	1.6	0.3	0	0	0.0	0	0.4	0.5
s8 255	0.00001 M H2SO4			5	6.2	5.6	6.5	0.0	0	0	0	0.1	0.1	0	0.02	0.0	0	0.4	0.1
s4 67	0.00001 M H2SO4	4.6	4.8	4.8	5.1	5.1		0.0	0	0	0	0.4	0.2						
s2 99	0.0001 M H2SO4	3.6	3.7	3.6	3.5	3.6		0.0	0	0	1	0.8	0.1						

s8 258	0.0001 M H_2SO_4			3.6	3.9	3.9	4.8	0.0	0	0	0	0.4	0.2	0	0.08	0.1	0	0.3	0.1
s4 234	0.0001 M H_2SO_4			3.5	4.1	3.9	4.7	0.0	0	0	0	0.4	0.4	0	0.05	0.0	0	0.6	0.5
S4-63	0.0001 M H_2SO_4	3.4				3.6		0.0	0	0	1	0.2	0.1						
S4-75	0.001 M H_2SO_4	2.6				2.8		0.0	0	0	0	0.5	0.2						
s4 235	0.001 M H_2SO_4			2.6	2.9	2.8	3.3	0.2	0.37	0.6	1	1.6	1	0	0.69	0.9	2	0.6	1.7
s8 256	0.001 M H_2SO_4			2.7	2.7	2.8	2.9	0.3	0.05	0.7	0	1.6	0.1	0.2	0.14	0.3	0	0.6	0.1
s2 87	0.001 M H_2SO_4	2.7	2.7	2.6	2.6	2.7		0.0	0	0	0	0.3	0.3						
s2 97	0.01 M H_2SO_4	1.8	2	1.9	1.9	2		0.3	0	0.3	0	0.4	0.1						
s8 253	0.01 M H_2SO_4			1.8	1.9	1.9	2.4	1.0	0.67	1.3	1	0.3	0.3	2	1.6	6.7	4	0.8	0.5
s6 247	0.01 M H_2SO_4			1.7	1.9	1.8	2.1	0.2	0.33	0.3	0	0.4	0.2	0.6	0.8	1.5	1	1.1	0.5
S4-73	0.01 M H_2SO_4	1.9				1.9		0.7	0.17	0.6	2	0.3	0.3						
S2-103	1 M NH_4NO_3	4.8				5.3		0.0	0	0	0	0.4	0.3						
s6 249	1 M NH_4NO_3			5.3	5.8	5.8	6.1	0.0	0	0.3	0	2.1	0.4	0	0	0.0	0	1.8	0.5
s8 261	1 M NH_4NO_3			5.3	6.4	5.5	5.7	0.0	0.14	0	0	0.6	0.6	0	0.34	0.0	0	0.8	0.5
s4 76	1 M NH_4NO_3	4.7	4.9	5	5	5.3		0.0	0	0	1	0.4	0.3						
s2 85	0.001 M NH_4NO_3	5.5	6.8	5.7	6.3	5.7		0.0	0	0	0	0	0						
s8 254	0.001 M NH_4NO_3			9.4	8.2	7.1	6.4	0.0	0	0	0	0	0.4	0	0	0.0	0	0.6	0.2
s6 241	0.001 M NH_4NO_3			6	7.2	6.5	6.4	0.0	0	0.3	0	0	0.1	0	0.05	0.0	0	0.7	0.1
S2-91	0.001 M NH_4NO_3	5.3				6.1		0.0	0	0	2	0.8	0.2						
S4-74	0.001M NH_3	9.2				8.6		0.0	0	0	1	0	0.2						
s6 245	0.001M NH_3			9	8.3	8.5	8.4	0.0	0	0	0	0	0.2	0	0	0.0	0	0.2	0.0
s8 252	0.001M NH_3			6.4	7.3	8.7	8.2	0.0	0	0	0	0	0.2	0	0	0.0	0	0.5	0.1
s4 71	0.001M NH_3	9.9	9.4	9.3	9.3	8.2		0.0	0	0	0	0.6	0.1						
s6 242	1M NH_3			11.4	11.8	11.6	11.6	0.0	0	0.7	3	0.9	0.2	0	0	1.8	3	0.6	0.2
s8 263	1M NH_3			11.6	11.8	11.8	11.6	0.0	0	1.2	5	1.5	0.4	0	0	4.0	3	0.4	0.5
s2 90	1M NH_3	11.7	11.6	11.6	11.5	11.7		0.0	0	0	3	0.7	0.1						
S4-78	1M NH_3	11.5				11.5		0.0	0	0.4	6	0.6	0.6						

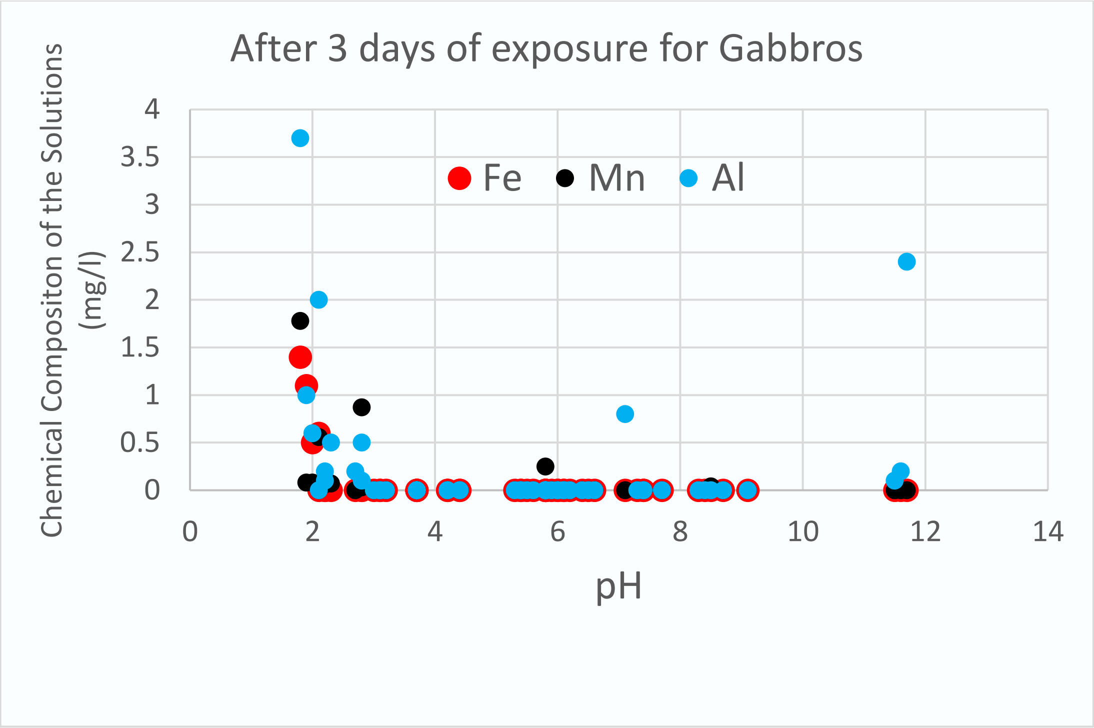


Figure 11 Chemical composition of the solutions (Fe, Mn and Al) versus pH after 3 days of exposure for the Gabbros. An identical scale is used for both gabbros and granophyres for the same exposure time and same measured elements.

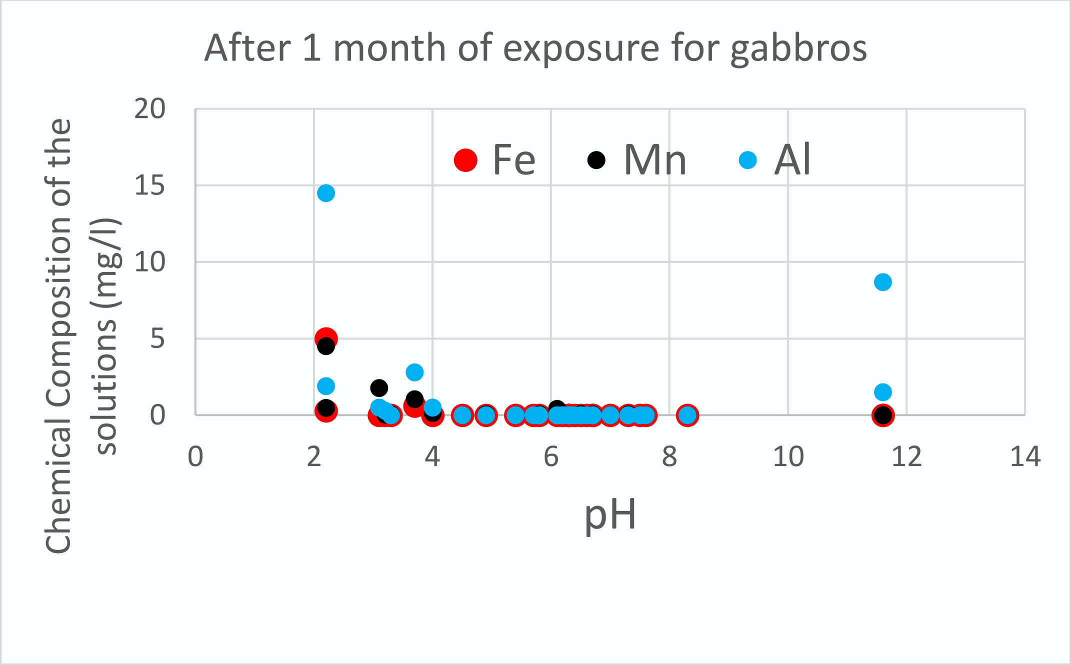


Figure 12 Chemical composition of the solutions (Fe, Mn and Al) versus pH after 1 month of exposure for the Gabbros. An identical scale is used for both gabbros and granophyres for the same exposure time and same measured elements.

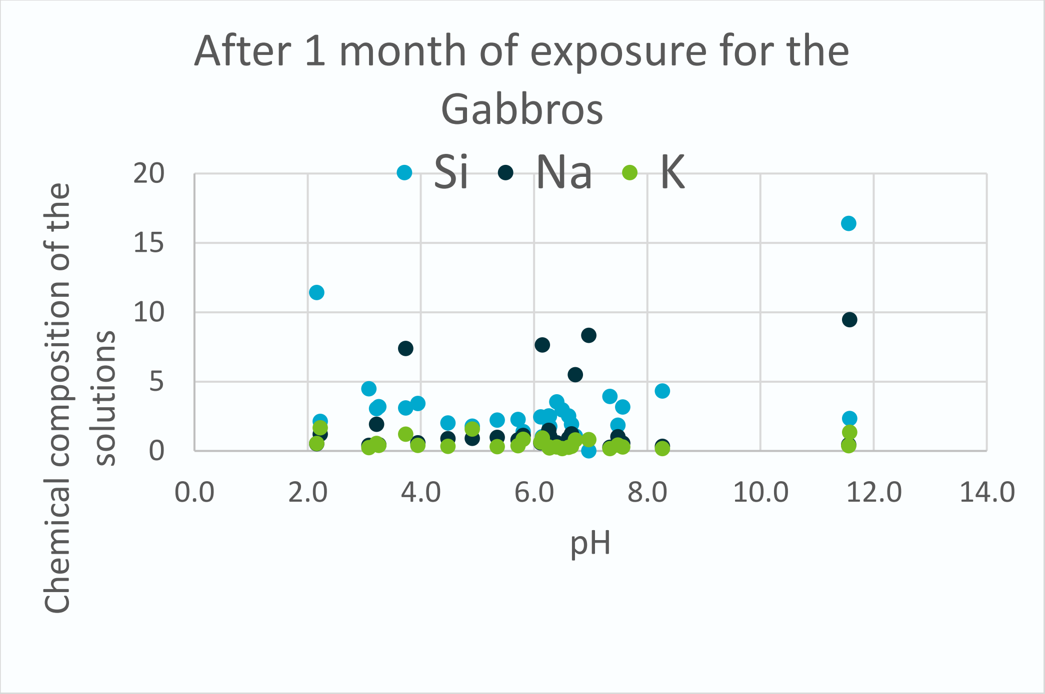


Figure 13 Chemical composition of the solutions (Si, Na and K) versus pH after 1 month of exposure for the Gabbros. An identical scale is used for both gabbros and granophyres for the same exposure time and same measured elements.

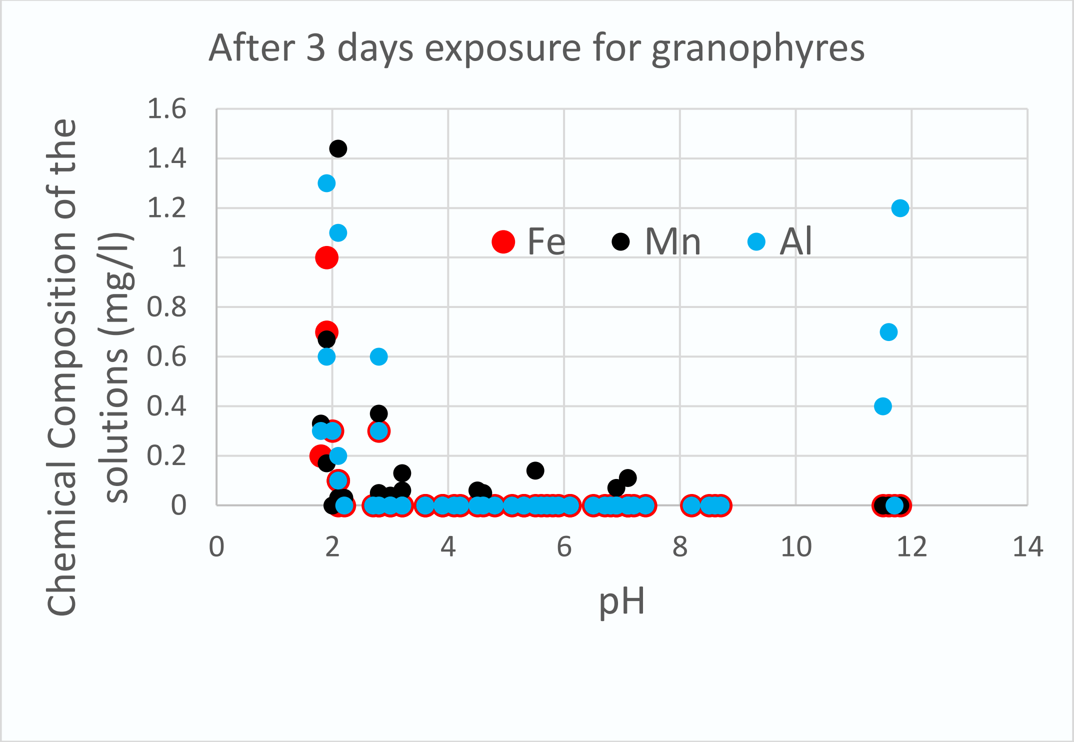


Figure 14 Chemical composition of the solutions (Fe, Mn and Al) versus pH after 3 days of exposure for the Granophyres. An identical scale is used for both gabbros and granophyres for the same exposure time and same measured elements.

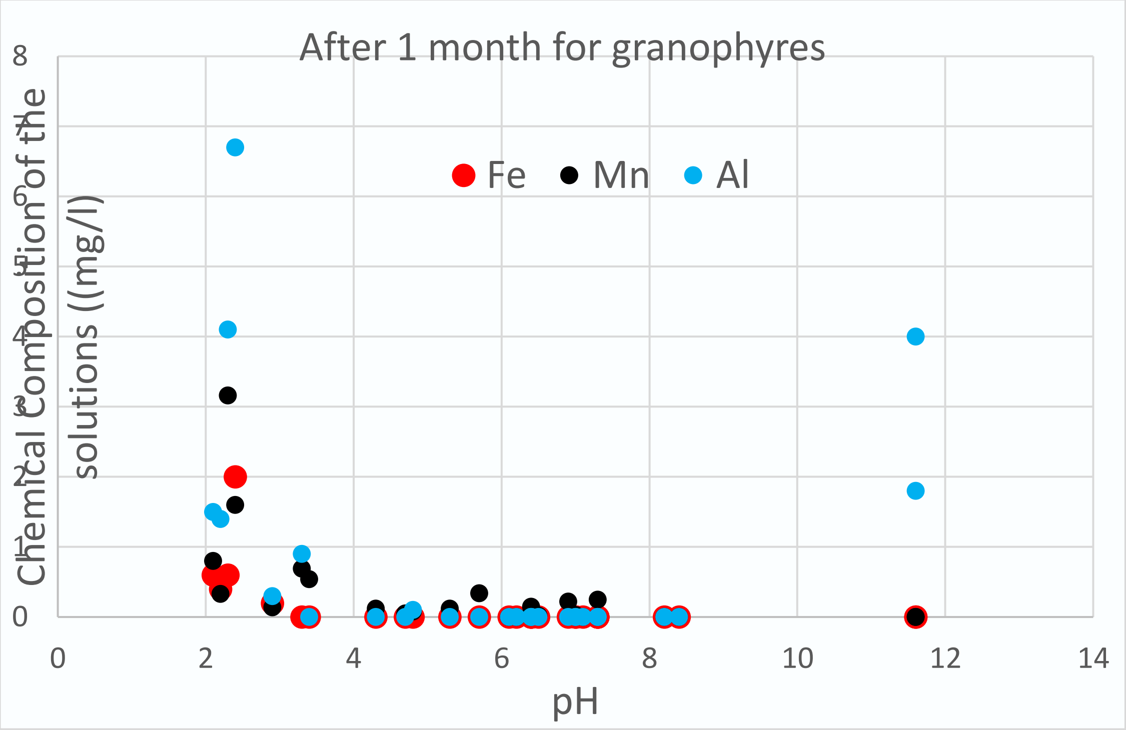


Figure 15 Chemical composition of the solutions (Fe, Mn and Al) versus pH after 1 month of exposure for the Granophyres. An identical scale is used for both gabbros and granophyres for the same exposure time and same measured elements.

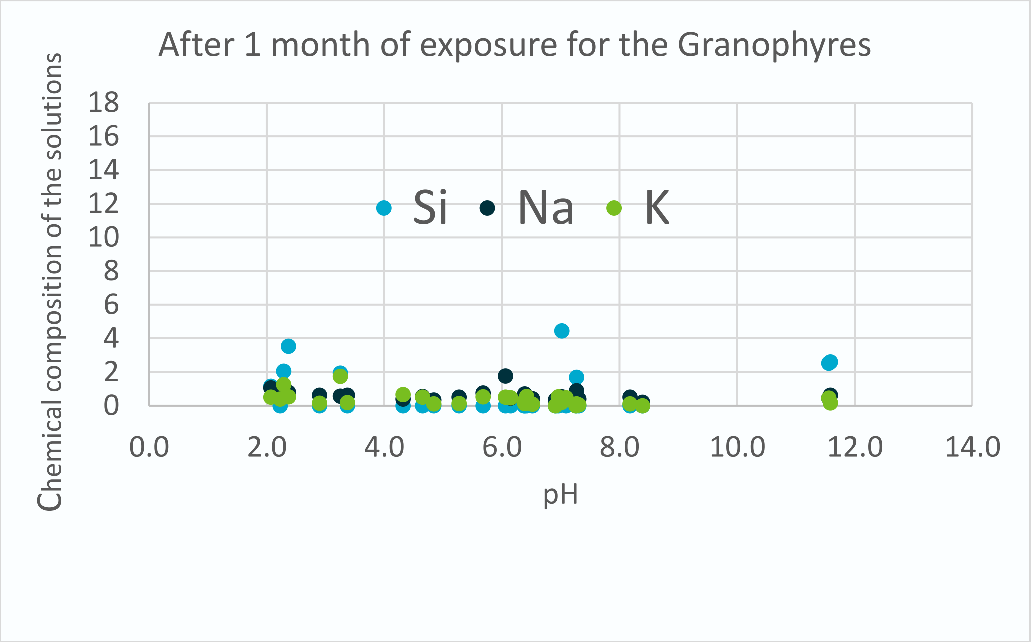


Figure 16 Chemical composition of the solutions (Si, Na and K) versus pH after 1 month of exposure for the Granophyres. An identical scale is used for both gabbros and granophyres for the same exposure time and same measured elements.

7.2 Optical Microscopy

Photographs were acquired before after exposure and documents surface features and colour. Note that in all cases, the resin has aged and became yellow. Only the extreme exposures have been shown here, the reminder of the optical photographies is displayed in Appendix 1 and 2. The solution containing 0.0111 M of H_2SO_4 has clearly affected the samples for both the gabbro (S1-35) and the granophyre (S4-69).

Table 11: Optical microscopy photographs for selected gabbros

Name	Before	After

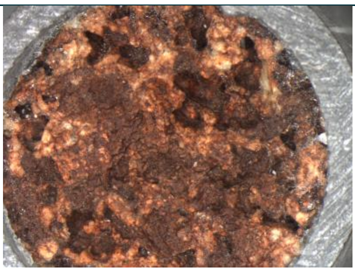
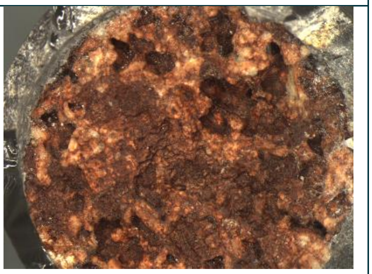
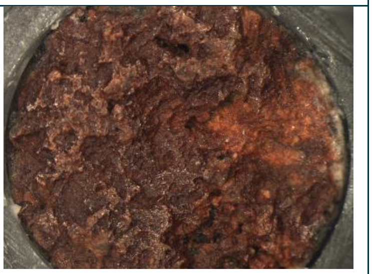
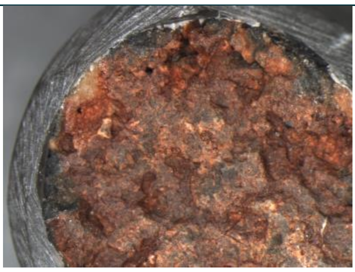
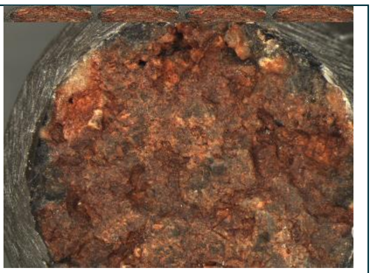
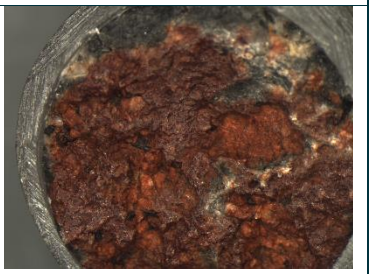
S1-29 H_2O		
S1-35 0.0111 M H_2SO_4		
S7-126 1M NH_3		

Table 12: Optical microscopy photographs for selected granophyres

Name	Before	After
S4-69 H_2O		

S2-97 0.0111 M H_2SO_4		
S2-90 1M NH_3		

7.3 Scanning Electron Microscopy Results

The SEM with EDXS provides qualitative chemical composition of rock surfaces. Ten identical areas were chosen on the backscattered picture and their chemical composition compared before and after exposure. Two examples are shown here, S1-29 (Table 13) exposed to distilled water (no dissolution observed in the solution) and S1-35 (Table 14) exposed to 0.0111 M H_2SO_4 (dissolution observed in the solution).

The comparison between the chemical composition before and after exposure for S1-29 (Table 15) and S1-35 (Table 16) was assessed by using a plus or minus one standard deviation (sigma). If the chemical composition of an element after exposure is outside this range, then it is significantly different from the chemical composition before exposure. This analysis was conducted for S1-29 (distilled water) and S1-35 (0.0111 M H_2SO_4) and shows that the EDX analyses cannot differentiate the sample that was unchanged (S1-29) and the sample that was changed (S1-35). The variability of the analyses is higher than the effect of the change.

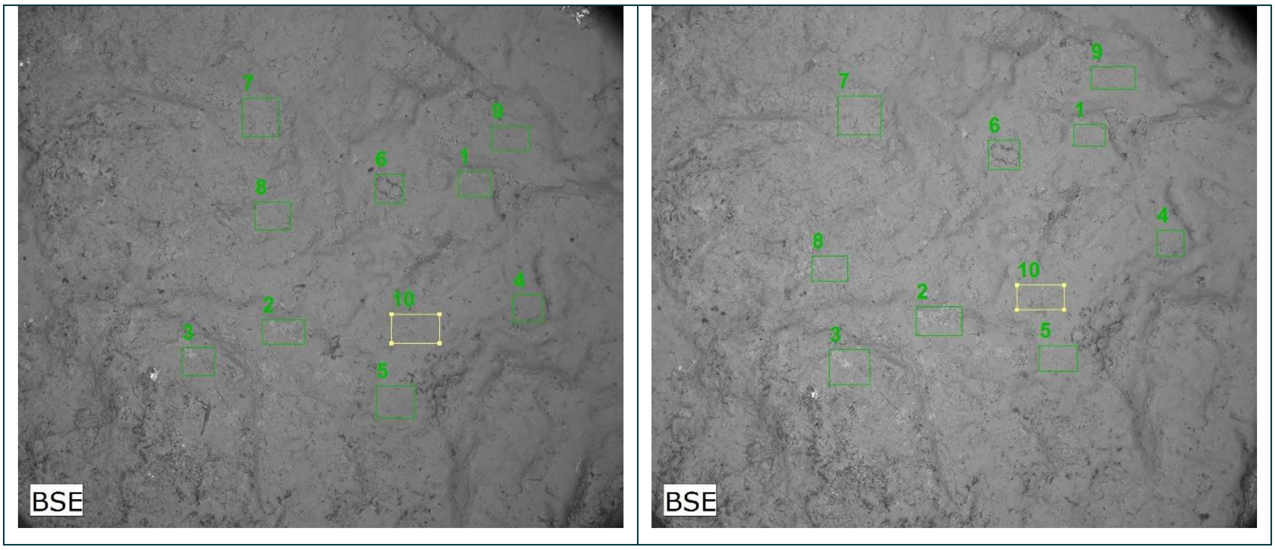


Table 13: Backscattered electron (BSE) image for S1-29, left before and right after exposure.

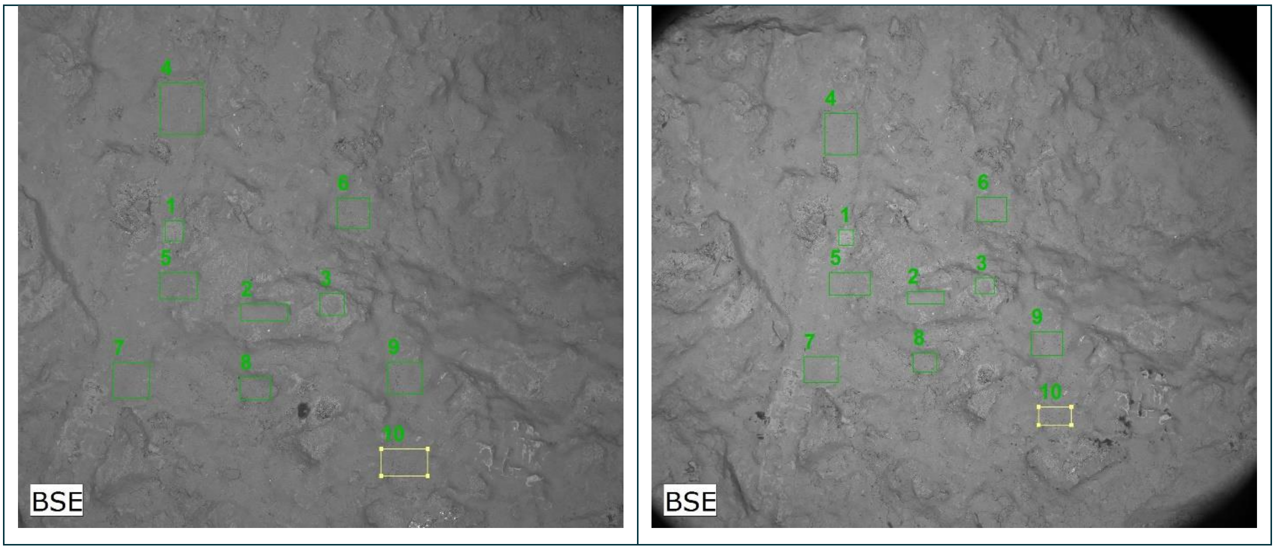


Table 14: Backscattered electron (BSE) image for S1-35, left before and right after exposure.

Table 15 Comparison between the chemical compositions (before in green) of the ten areas shown in Table 13 for samples S1-29. If the chemical composition after exposure is significantly different from the composition before exposure, the number is in red.

Oxides	Comp. wt.%	Sigma wt.%	Minus	Plus	Comp. wt.%	Oxides	Comp. wt.%	Sigma wt.%	Minus	Plus	Comp. wt.%
SiO_2	46.38	2.34	44.04	48.72	48.09	Al2O3	27.4	1.92	25.48	29.32	27.6
Al_2O_3	27.59	1.8	25.79	29.39	28.94	SiO2	48.61	2.63	45.98	51.24	48.85
FeO	17.6	0.9	16.7	18.5	16.35	P2O5	0.42	0.11	0.31	0.53	0.71
CaO	3.47	0.26	3.21	3.73	2.12	Na2O	0.42	0.15	0.27	0.57	0.31
K_2O	1.49	0.17	1.32	1.66	0.94	MgO	1.63	0.24	1.39	1.87	1.58
MgO	1.58	0.22	1.36	1.8	1.69	K2O	0.89	0.14	0.75	1.03	1.37
Na_2O	0.67	0.17	0.5	0.84	0.44	CaO	0.83	0.13	0.7	0.96	0.62
TiO_2	0.82	0.12	0.7	0.94	0.66	TiO2	1.04	0.13	0.91	1.17	1.04
P_2O_5	0.32	0.1	0.22	0.42	0.68	MnO	0.12	0.09	0.03	0.21	0.14
MnO	0.09	0.09	0	0.18	0.1	FeO	18.63	1.01	17.62	19.64	17.79
Al_2O_3	25.97	1.92	24.05	27.89	26.2	Al2O3	28.98	1.87	27.11	30.85	28.24
SiO_2	47.03	2.69	44.34	49.72	47.52	SiO2	50.15	2.51	47.64	52.66	48.67
P_2O_5	0.76	0.12	0.64	0.88	0.71	P2O5	0.68	0.11	0.57	0.79	0.69
Na_2O	0.78	0.21	0.57	0.99	0.48	Na2O	0.5	0.15	0.35	0.65	0.31
MgO	2.36	0.31	2.05	2.67	2.25	MgO	1.82	0.23	1.59	2.05	1.69
K_2O	0.9	0.14	0.76	1.04	1.5	K2O	1.44	0.17	1.27	1.61	1.05
CaO	0.61	0.12	0.49	0.73	0.82	CaO	0.7	0.11	0.59	0.81	0.59
TiO_2	0.87	0.12	0.75	0.99	1.13	TiO2	0.63	0.1	0.53	0.73	0.89
MnO	0.03	0.08	-0.05	0.11	0.09	MnO	0.06	0.08	-0.02	0.14	0.01
FeO	20.69	1.17	19.52	21.86	19.3	FeO	15.04	0.77	14.27	15.81	17.86
Al_2O_3	28.95	1.94	27.01	30.89	28.38	Al2O3	27.68	2	25.68	29.68	28.59
SiO_2	49.35	2.56	46.79	51.91	48.11	SiO2	46.77	2.62	44.15	49.39	49.2
P_2O_5	1	0.13	0.87	1.13	0.85	P2O5	0.59	0.11	0.48	0.7	1.07
Na_2O	0.73	0.19	0.54	0.92	0.46	Na2O	0.51	0.16	0.35	0.67	0.66
MgO	1.92	0.25	1.67	2.17	1.8	MgO	1.73	0.25	1.48	1.98	1.89
K_2O	1.18	0.16	1.02	1.34	0.88	K2O	1.49	0.18	1.31	1.67	1.06
CaO	1.17	0.14	1.03	1.31	0.75	CaO	0.74	0.12	0.62	0.86	0.53

TiO_2	0.62	0.11	0.51	0.73	0.73
MnO	0.04	0.08	-0.04	0.12	0
FeO	15.04	0.8	14.24	15.84	18.03
Al_2O_3	30.12	2.13	27.99	32.25	29.46
SiO_2	52.53	2.87	49.66	55.4	51.13
P_2O_5	0.95	0.13	0.82	1.08	1.22
Na_2O	0.62	0.18	0.44	0.8	0.69
MgO	2.06	0.27	1.79	2.33	2.24
K_2O	1.49	0.18	1.31	1.67	1.36
CaO	0.68	0.12	0.56	0.8	0.56
TiO_2	0.5	0.1	0.4	0.6	0.81
MnO	0.04	0.08	-0.04	0.12	0.05
FeO	11.01	0.64	10.37	11.65	12.49
SiO_2	49.67	2.93	46.74	52.6	49.8
Al_2O3	30.03	2.28	27.75	32.31	30.32
FeO	13.18	0.8	12.38	13.98	13.06
MgO	2.2	0.3	1.9	2.5	2.19
K_2O	1.49	0.19	1.3	1.68	1.17
CaO	0.83	0.13	0.7	0.96	0.81
TiO_2	0.79	0.12	0.67	0.91	0.74
Na_2O	0.75	0.2	0.55	0.95	0.6
P_2O_5	0.99	0.13	0.86	1.12	1.27
MnO	0.05	0.08	-0.03	0.13	0.04

TiO2	0.96	0.13	0.83	1.09	0.74
MnO	0.1	0.09	0.01	0.19	0.09
FeO	19.42	1.08	18.34	20.5	16.18
Al2O3	29.06	2.3	26.76	31.36	29.72
SiO2	47.64	2.93	44.71	50.57	49.3
P2O5	0.96	0.13	0.83	1.09	1.15
Na2O	0.73	0.2	0.53	0.93	0.55
MgO	2.1	0.3	1.8	2.4	2.06
K2O	1.35	0.18	1.17	1.53	1.03
CaO	0.72	0.13	0.59	0.85	0.6
TiO2	0.86	0.13	0.73	0.99	0.8
MnO	0.11	0.09	0.02	0.2	0.02
FeO	16.48	1.02	15.46	17.5	14.77
Al2O3	30.09	2.05	28.04	32.14	28.83
SiO2	50.23	2.66	47.57	52.89	48.22
P2O5	0.79	0.12	0.67	0.91	0.96
Na2O	1.89	0.25	1.64	2.14	0.45
MgO	0.52	0.15	0.37	0.67	1.95
CaO	1.18	0.15	1.03	1.33	0.55
K2O	0.69	0.12	0.57	0.81	1.02
TiO2	0.72	0.11	0.61	0.83	0.83
MnO	0.04	0.08	-0.04	0.12	0.09
FeO	13.85	0.75	13.1	14.6	17.1

Table 16 Comparison between the chemical compositions (before in green) of the ten areas shown in Table 13 for samples S1-35. If the chemical composition after exposure is significantly different from the composition before exposure, the number is in red.

Oxides	Comp. wt.%	Sigma wt.%	Minus	Plus	Comp. wt.%	Oxides	Comp. wt.%	Sigma wt.%	Minus	Plus	Comp. wt.%
Al_2O3	21.69	1.62	20.07	23.31	20.75	Al2O3	25.2	1.97	23.23	27.2	26.71
SiO_2	44.5	2.54	41.96	47.04	42.42	SiO2	49.33	2.98	46.35	52.3	53.85
P_2O_5	0.94	0.14	0.8	1.08	0.83	P2O5	0.38	0.11	0.27	0.49	0.5
Na_2O	0.59	0.2	0.39	0.79	0.5	Na2O	0.55	0.19	0.36	0.74	0.2
MgO	2.24	0.32	1.92	2.56	1.86	MgO	2.04	0.3	1.74	2.34	1.58
K_2O	1.34	0.19	1.15	1.53	0.84	K2O	1.54	0.2	1.34	1.74	1.79
CaO	2.1	0.21	1.89	2.31	0.56	CaO	1.51	0.18	1.33	1.69	0.55
TiO_2	1.23	0.15	1.08	1.38	1.45	TiO2	1.01	0.14	0.87	1.15	1.2
MnO	0.06	0.09	-0.03	0.15	0.16	MnO	0.17	0.1	0.07	0.27	0.03
FeO	25.32	1.41	23.91	26.73	30.62	FeO	18.25	1.1	17.15	19.4	13.58
Al2O3	24.88	1.81	23.07	26.69	25.71	Al2O3	25.72	1.79	23.93	27.5	26.28
SiO_2	51.16	2.87	48.29	54.03	52.4	SiO2	52.05	2.8	49.25	54.9	53.68
P_2O_5	0.26	0.1	0.16	0.36	0.28	P2O5	0.36	0.1	0.26	0.46	0.66
Na_2O	0.53	0.17	0.36	0.7	0.29	Na2O	0.73	0.19	0.54	0.92	0.53
MgO	1.91	0.27	1.64	2.18	1.49	MgO	1.98	0.26	1.72	2.24	1.68
K_2O	1.17	0.16	1.01	1.33	1.49	K2O	1.5	0.18	1.32	1.68	1.06
CaO	1.77	0.18	1.59	1.95	0.75	CaO	1.95	0.19	1.76	2.14	0.75
TiO_2	1.08	0.13	0.95	1.21	1.05	TiO2	0.87	0.12	0.75	0.99	0.76
MnO	0.19	0.1	0.09	0.29	0.09	MnO	0.07	0.08	-0.01	0.15	0.04
FeO	17.06	0.97	16.09	18.03	16.45	FeO	14.77	0.81	13.96	15.6	14.56
Al_2O3	26.9	2.03	24.87	28.93	27.83	SiO2	54.61	3.08	51.53	57.7	56.13
SiO_2	47.09	2.75	44.34	49.84	49.27	P2O5	0.58	0.11	0.47	0.69	0.81
P_2O_5	0.34	0.1	0.24	0.44	0.59	Al2O3	25.22	1.85	23.37	27.1	24.35
Na_2O	1.3	0.29	1.01	1.59	1.2	Na2O	1.06	0.24	0.82	1.3	1.08
MgO	1.63	0.25	1.38	1.88	1.3	MgO	1.89	0.26	1.63	2.15	1.62
K_2O	0.8	0.14	0.66	0.94	0.6	K2O	1	0.15	0.85	1.15	0.72

CaO	11.78	0.76	11.02	12.54	10.72	CaO	2.97	0.25	2.72	3.22	1.83
TiO2	0.33	0.1	0.23	0.43	0.45	TiO2	0.57	0.11	0.46	0.68	0.77
MnO	0.08	0.09	-0.01	0.17	0.04	MnO	0.02	0.08	-0.06	0.1	0.1
FeO	9.76	0.62	9.14	10.38	8	FeO	12.08	0.71	11.37	12.8	12.59
Al$_2$O3	26.34	1.76	24.58	28.1	26.69	Al2O3	26.02	1.68	24.34	27.7	26.39
SiO$_2$	51.05	2.63	48.42	53.68	51.12	P2O5	0.39	0.1	0.29	0.49	0.84
P$_2$O$_5$	0.31	0.09	0.22	0.4	0.56	SiO2	54.09	2.69	51.4	56.8	53.91
Na$_2$O	0.61	0.16	0.45	0.77	0.47	Na2O	0.64	0.17	0.47	0.81	0.65
MgO	2.18	0.26	1.92	2.44	1.95	MgO	2.07	0.25	1.82	2.32	1.89
K$_2$O	1.03	0.14	0.89	1.17	1.37	K2O	1.35	0.16	1.19	1.51	1.04
CaO	1.61	0.16	1.45	1.77	0.39	CaO	1.53	0.16	1.37	1.69	0.54
TiO$_2$	0.85	0.11	0.74	0.96	0.91	TiO2	0.61	0.1	0.51	0.71	0.82
MnO	0.04	0.08	-0.04	0.12	0.04	MnO	0.09	0.08	0.01	0.17	0.02
FeO	15.97	0.83	15.14	16.8	16.5	FeO	13.22	0.69	12.53	13.9	13.88
Al$_2$O3	26.01	1.93	24.08	27.94	26.85	SiO2	51.16	2.78	48.38	53.9	52.68
SiO$_2$	48.27	2.76	45.51	51.03	51.18	Al2O3	26.68	1.88	24.8	28.6	27.22
P$_2$O$_5$	0.29	0.1	0.19	0.39	0.57	P2O5	0.56	0.11	0.45	0.67	0.86
MgO	1.9	0.27	1.63	2.17	0.53	Na2O	0.75	0.19	0.56	0.94	0.6
Na$_2$O	0.57	0.18	0.39	0.75	1.84	MgO	2.12	0.27	1.85	2.39	1.98
K$_2$O	1.95	0.22	1.73	2.17	1.12	K2O	1.16	0.16	1	1.32	1.38
CaO	4.1	0.32	3.78	4.42	2.35	CaO	1.3	0.15	1.15	1.45	0.38
TiO$_2$	0.78	0.12	0.66	0.9	0.87	TiO2	0.7	0.11	0.59	0.81	0.78
MnO	0.09	0.09	0	0.18	0.01	MnO	0.03	0.08	-0.05	0.11	0.04
FeO	16.05	0.93	15.12	16.98	14.67	FeO	15.54	0.86	14.68	16.4	14.08

7.4 KM Colour results

The samples were measured with the KM photospectrometer before and after exposure and L, a, and b parameters were extracted. The L, a, and b parameters were statistically analysed to assess if there was a significant difference between before and after the various chemical exposures. A t-Test with two-sample assuming equal variances was used and we used P (T<=t) two-tail as the best way of assessing a potential difference between before and after exposure. It is expected that a significant difference will be observed where Fe, Mn and/or Al are present in the solutions corresponding to the most concentrated liquids. On the other hand, for distilled water or weak solutions where Fe, Mn and/or Al are not present in the solutions, the expectation is that no significant change would be calculated.

For the KM data, the P (T<=t) two-tail was generally less than 0.05 (Table 17) meaning that there was no significant difference before and after all exposures for only 7 seven samples out of 26 samples (Table 17). A significant difference was observed for 19 samples. A difference in L, a and b was observed for sample S1-29 immersed in distilled water which is unexpected as no Fe, Mn or Al was measured the solution. A difference in L only but no in a and b parameters was observed for sample S4-69 also immersed in distilled water which is also unexpected as no Fe, Mn or Al was measured the solution. Overall, 19 samples show significant difference before and after all exposures regardless of the aggressiveness of the solution as we see significant difference for samples in distilled water and samples in various concentrations of nitric and sulfuric acid as well as ammonia and ammonium nitrate. The L, a and b parameters cannot accurately discriminate between samples that have shown no dissolution and samples that have shown dissolution after exposure.

7.5 ASD Spectral Results

The samples were measured with the ASD spectrometer before and after exposure and spectral parameters were extracted. They are seven parameters and include the depth of the 900 nm absorption, the minimum wavelength of the 900 nm absorption, the depth of the chlorite and kaolinite absorption, L, a, and b. These parameters were statistically analysed to assess if there was a significant difference between before and after the various chemical exposures. A t-Test with two-sample assuming equal variances was used and we used P (T<=t) two-tail as the best way of assessing a potential difference between before and after exposure (Table 18). As shown for the KM Photospectrometer, it is expected that a significant difference will be observed where Fe, Mn and/or Al are present in the solutions corresponding to the most concentrated liquids. On the other hand, for distilled water or weak solutions where Fe, Mn and/or Al are not present in the solutions, the expectation is that no significant change would be calculated.

The seven ASD parameters for the samples submerged in water (S1-29) for the gabbro and S4-69 for the granophyre show no significant change, P (T<=t) two-tail is more than 0.05, an expected result.

For the depth of the 900 nm absorption, 3 values (S1-83, S1-2 and S1-28) out of 26 are significant however, they do not correspond to the solutions with Fe, Mn and/or Al are in solution. For the minimum wavelength of the 900 nm absorption, six values (S1-33, S1-10, S7-126, S7-135, S2-96 and S2-99) out of 26 are significant. Only two (S1-10 and S7-126) correspond to solution with dissolved Al.

For the depth of the chlorite absorption, three values (S1-2, S1-34 and S4-80) out of 26 are significant however, only S4-80 correspond to the solutions with dissolved Mn.

For the depth of the kaolinite absorption, three values (S1-2, S7-126 and S2-90) out of 26 are significant however, only S7-126 correspond to the solutions with dissolved Al.

For the L parameter, seventeen values out of 26 are significant however, only five correspond to the solutions with dissolved Fe, Mn and/or Al (S1-35[Fe, Mn &Al], S7-126 [Al], S4-80 [Mn], S4-62 [Mn & Al] and S2-97 [Fe& Al]. The twelve remaining samples show a significant difference after exposure with corresponding dissolution of Fe, Mn and/or Al.

For the a parameter, ten values out of 26 are significant however, only five correspond to the solutions with dissolved Fe, Mn and/or Al (S1-35[Fe, Mn &Al], S7-126 [Al], S4-80 [Mn] and S2-97 [Fe& Al]. The six remaining samples show a significant difference after exposure with corresponding dissolution of Fe, Mn and/or Al.

For the b parameter, seventeen values out of 26 are significant however, only five correspond to the solutions with dissolved Fe, Mn and/or Al (S1-10 [Al], S1-35[Fe, Mn &Al], S7-126 [Al], S4-62 [Mn & Al] and S2-97 [Fe& Al]. The twelve remaining samples show a significant difference after exposure with corresponding dissolution of Fe, Mn and/or Al.

None of these parameters can accurately discriminate between samples that have genuinely been dissolved (as demonstrated by Fe, Mn and/or Al) in solution.

Table 17. Statistical analyses of the KM derived L, a and b parameters. P two tails less than 0.05 (in Red) shows significance difference between before and after exposure. In orange, solutions containing Fe, Mn or Al.

		pH					3 Days (mg/l)								
	Solutions	**Initial**	**4 h**	**1 day**	**2 days**	**3 days**	**Fe**	**Mn**	**Al**	**Si**	**Na**	**K**	L	a	b
S1-29	H2O	6.3	5.6	6.8	5.9	6.2	0	0	0	0	0.3	0.1	0.0000	0.0000	0.0000
S1-33	0.00001 M HNO3	4.9	5.1	5.9	5.7	5.4	0	0	0	0	0	0	0.0000	0.0000	0.0000
S1-24	0.0001 M HNO3	4	4	4.2	4.2	4.2	0	0	0	0	0	0	0.0000	0.0000	0.1255
S1-83	0.001 M HNO3	3	3	3	2.9	3	0	0	0	0	0.3	0.1	0.0058	0.0000	0.0000
S1-47	0.01 M HNO3	2.1	2.2	2.1	2	2.1	0	0	0	0	0.3	0.2	0.0154	0.0000	0.0000
S1-2	0.00001 M H2SO4	4.6	4.7	5.2	5.3	5.3	0	0	0	0	0.7	0.2	0.0000	0.0000	0.0000
S1-34	0.0001 M H2SO4	3.6	3.6	3.7	3.6	3.7	0	0	0	1	1	0.3	0.0000	0.0000	0.0004
S1-10	0.001 M H2SO4	2.7	2.7	2.7	2.5	2.7	0	0	0.2	1	0.3	0.2	0.0000	0.0004	0.0000
S1-35	0.01 M H2SO4	1.8	2	1.9	1.8	2	0.5	0.08	0.6	2	0.6	0.3	0.0000	0.0000	0.0000
S1-28	1 M NH4NO3	4.7	4.9	5.4	5.5	5.8	0	0	0	0	0.3	0.2	0.0004	0.0031	0.0000
S1-9	0.001 M NH4NO3	5.5	5.7	5.9	6	6	0	0	0	0	0.3	0.2	0.2416	0.0001	0.0001
S7-126	1M NH3	11.7	11.6	11.6	11.5	11.6	0	0	0.2	6	0.3	0.7	0.0000	0.0000	0.0011
S7-135	0.001M NH3	9.9	9.3	9.4	9.2	9.1	0	0	0	0	0.5	0.2	0.0000	0.0415	0.0000
S4-69	H2O	6.3	8.4	7.1	7.2	6.9	0	0	0	0	0.3	0	0.0000	0.3877	0.9704
S2-96	0.00001 M HNO3	4.9	7.6	6.8	6.6	6.1	0	0	0	0	0.5	0.1	0.0298	0.0362	0.0000
S2-83	0.0001 M HNO3	4	4.1	4.1	4.1	4.2	0	0	0	1	0	0	0.0000	0.0000	0.0000
S4-80	0.001 M HNO3	3	3.1	2.9	3	3	0	0.04	0	0	0.4	0.3	0.0385	0.0002	0.0000
S4-62	0.01 M HNO3	2.1	2.2	2.1	2	2.1	0	0.03	0.1	1	0	0.2	0.0000	0.0103	0.0055
S4-67	0.00001 M H2SO4	4.6	4.8	4.8	5.1	5.1	0	0	0	0	0.4	0.2	0.2762	0.0001	0.0000
S2-99	0.0001 M H2SO4	3.6	3.7	3.6	3.5	3.6	0	0	0	1	0.8	0.1	0.0000	0.0689	0.0003
S2-87	0.001 M H2SO4	2.7	2.7	2.6	2.6	2.7	0	0	0	0	0.3	0.3	0.0000	0.0004	0.0000
S2-97	0.01 M H2SO4	1.8	2	1.9	1.9	2	0.3	0	0.3	0	0.4	0.1	0.0000	0.0000	0.0000
S4-76	1 M NH4NO3	4.7	4.9	5	5	5.3	0	0	0	1	0.4	0.3	0.0002	0.0000	0.0000
S2-85	0.001 M NH4NO3	5.5	6.8	5.7	6.3	5.7	0	0	0	0	0	0	0.0000	0.0007	0.1064
S2-90	1M NH3	11.7	11.6	11.6	11.5	11.7	0	0	0	3	0.7	0.1	0.0000	0.0609	0.0040
S4-71	0.001M NH3	9.9	9.4	9.3	9.3	8.2	0	0	0	0	0.6	0.1	0.0000	0.0000	0.0000

Table 18. Statistical analyses of the ASD derived parameters. P two tails less than 0.05 (in Red) shows significance difference between before and after exposure. In orange, solutions containing Fe, Mn or Al.

				pH					3 Days (mg/l)						P(T<=t) two-tail				
	Solutions	**Initial**	**4 h**	**1 day**	**2 days**	**3 days**	**Fe**	**Mn**	**Al**	**Si**	**Na**	**K**	**Depth 900nm**	**MinWav 900nm**	**Depth Chlorite**	**Depth Kaol**	**L**	**a**	**b**
S1-29	H2O	6.3	5.6	6.8	5.9	6.2	0	0	0	0	0.3	0.1	0.09	0.64	0.94	0.97	0.31	0.9	0.94
S1-33	0.00001 M HNO3	4.9	5.1	5.9	5.7	5.4	0	0	0	0	0	0	0.39	0.01	0.55	0.52	0	0.09	0.23
S1-24	0.0001 M HNO3	4	4	4.2	4.2	4.2	0	0	0	0	0	0	0.25	0.96	0.45	0.16	0.61	0.75	0.51
S1-83	0.001 M HNO3	3	3	3	2.9	3	0	0	0	0	0.3	0.1	0.03	0.33	0.73	0.87	0.04	0.26	0.05
S1-47	0.01 M HNO3	2.1	2.2	2.1	2	2.1	0	0	0	0	0.3	0.2	0.13	0.34	0.98	0.48	0.08	0.21	0
S1-2	0.00001 M H2SO4	4.6	4.7	5.2	5.3	5.3	0	0	0	0	0.7	0.2	0	0.77	0.05	0	0	0.19	0
S1-34	0.0001 M H2SO4	3.6	3.6	3.7	3.6	3.7	0	0	0	1	1	0.3	0.25	0.12	0.05	0.62	0.88	0.31	0.99
S1-10	0.001 M H2SO4	2.7	2.7	2.7	2.5	2.7	0	0	0.2	1	0.3	0.2	0.66	0.02	0.4	0.19	0.6	0.06	0.01
S1-35	0.01 M H2SO4	1.8	2	1.9	1.8	2	0.5	0.08	0.6	2	0.6	0.3	0.26	0.13	0.81	0.91	0	0	0
S1-28	1 M NH4NO3	4.7	4.9	5.4	5.5	5.8	0	0	0	0	0.3	0.2	0.03	0.66	0.68	0.48	0.6	0.13	0.01
S1-9	0.001 M NH4NO3	5.5	5.7	5.9	6	6	0	0	0	0	0.3	0.2	0.37	0.89	0.74	0.76	0	0	0
S7-126	1M NH3	11.7	11.6	11.6	11.5	11.6	0	0	0.2	6	0.3	0.7	0.12	0.03	0.66	0.03	0	0.02	0
S7-135	0.001M NH3	9.9	9.3	9.4	9.2	9.1	0	0	0	0	0.5	0.2	0.9	0.04	0.88	0.3	0	0.01	0
S4-69	H2O	6.3	8.4	7.1	7.2	6.9	0	0	0	0	0.3	0	0.25	0.46	0.54	0.42	0.11	0.46	0.94
S2-96	0.00001 M HNO3	4.9	7.6	6.8	6.6	6.1	0	0	0	0	0.5	0.1	0.54	0	0.76	0.09	0	0.15	0.14
S2-83	0.0001 M HNO3	4	4.1	4.1	4.1	4.2	0	0	0	1	0	0	0.22	0.61	0.53	0.34	0.37	0.05	0.31
S4-80	0.001 M HNO3	3	3.1	2.9	3	3	0	0.04	0	0	0.4	0.3	0.38	0.3	0.02	0.19	0	0.02	0.07
S4-62	0.01 M HNO3	2.1	2.2	2.1	2	2.1	0	0.03	0.1	1	0	0.2	0.51	0.26	0.57	0.91	0.02	0.17	0.02
S4-67	0.00001 M H2SO4	4.6	4.8	4.8	5.1	5.1	0	0	0	0	0.4	0.2	0.21	0.64	0.29	0.97	0	0.16	0
S2-99	0.0001 M H2SO4	3.6	3.7	3.6	3.5	3.6	0	0	0	1	0.8	0.1	0.62	0.01	0.83	0.32	0.01	0.41	0.05
S2-87	0.001 M H2SO4	2.7	2.7	2.6	2.6	2.7	0	0	0	0	0.3	0.3	0.7	0.99	0.93	0.22	0	0.01	0
S2-97	0.01 M H2SO4	1.8	2	1.9	1.9	2	0.3	0	0.3	0	0.4	0.1	0.44	0.74	0.15	0.06	0	0	0
S4-76	1 M NH4NO3	4.7	4.9	5	5	5.3	0	0	0	1	0.4	0.3	0.9	0.19	0.38	0.82	0	0.07	0.05
S2-85	0.001 M NH4NO3	5.5	6.8	5.7	6.3	5.7	0	0	0	0	0	0	0.29	0.65	0.34	0.74	0.27	0.84	0.24
S2-90	1M NH3	11.7	11.6	11.6	11.5	11.7	0	0	0	3	0.7	0.1	0.69	0.54	0.19	0.01	0	0	0
S4-71	0.001M NH3	9.9	9.4	9.3	9.3	8.2	0	0	0	0	0.6	0.1	0.62	0.35	0.45	0.08	0	0	0

8. DISCUSSION AND CONCLUSION

This preliminary study using novel sample preparation methods to provide a new approach to determining the effects of solutions of different compositions and concentrations on rock weathering. As a scoping tool, it is very valuable in targeting future work. It is not intended to serve as an exhaustive or definitive analysis of the impacts of the chosen leach solutions on granophyre and gabbro rocks. Nor was it intended as an indication for permissible pollution levels.

The extreme weathering experiment conducted here on weathered samples of gabbro and granophyres, exposed to the thirteen (13) different solutions is aimed at understanding what could happen to the Burrup Peninsula/Murujuga rocks under various exposure conditions. One hundred and twenty six (126) rock cylinders from all original seven sites of the Burrup Peninsula/Murujuga Monitoring program (Duffy et al., 2017) were prepared for this study. They include fifty-five (55) gabbro samples from Site 1 (45 drilled samples) and Site 7 (10 drilled samples) and fifty-five (55) granophyre samples from Sites 2 (12 drilled samples), Site 4 (22 drilled samples), Site 5 (two (2) drilled samples), Site 6 (seven (7) drilled samples) and Site 8 (12 drilled samples). Four samples of gabbros and four samples of granophyres were subjected to a similar solution to provide more representativity.

All samples were prepared in such a way that only the surface of the sample (110 weathered surface and 16 fresh surface cylinders) was in contact with the different solutions. All the samples were immersed in reaction vessels at 50°C with 5 solutions including: (1) distilled water (control); (2)nitric acid (0.00001 M pH 4.4, 0.0001 M pH 3.6, 0.001 M pH 2.8 and 0.0087M pH 2.0); (3) sulphuric acid (0.00001 M pH 4.3, 0.0001 M pH 3.4, 0.001 M pH 2.6 and 0.011M pH 1.9); (4) ammonium nitrate (0.001 M pH 4.8 and 1M pH 5.3) and (5) ammonia (0.001M pH 9.2 and 1M pH 11.5). The solutions were heated at 50°C as this temperature can be reached on the surface of the rock in summer in the Burrup Peninsula/Murujuga. This temperature also increases the kinetics of the reaction. Fifty eight (58) solutions were also measured after 1-month exposure.

Some of the concentrations and temperature for the weathering experiment are extreme conditions but they provide a guide for assessing potential damage to the weathered gabbros and granophyres of the Burrup Peninsula/Murujuga and in turn, the potential damage to the petroglyphs.

For the majority of the gabbros and after 3 days at 50°C, dissolution starts either at pH 3 or below for Al, Mn and Fe or more than pH 11 for Al. Some outlier results were also observed for S1-225 and S7-206 showing some dissolution of Mn (0.07 for both) in distilled water at neutral pH (7). It is rather unexpected to see such results as it would mean that under rainwater (pH = 5.5), Mn will be dissolved in natural condition which is clearly not the case, as otherwise, Mn would not be present on the surface of the Burrup weathered rocks as they have been subjected to thousands of years of rain. The other five samples exposed in distilled water show no dissolved Mn. Another outlier is S1-43 that shows no Mn in solution at pH 3.7 after 3 days but 0.07 after a month at pH 4.9; a similar concentration found for Mn in distilled water. The last two outliers are S1-14 and S7-203 showing dissolved Mn (respectively 0.06 and 0.25) at pH 5.8. Again a much unexpected result as it would mean that under rainwater (pH = 5.5), Mn will be dissolved in natural condition which is clearly not the case as mentioned above.

For the majority of the granophyres and after 3 days at 50°C, dissolution starts at pH 3.2 and below for Al, Mn and Fe or more than pH 11 for Al. Some outlier results were also observed for S4-66 and S6-244 showing some dissolution of Mn in distilled water at neutral pH (7) up to 0.25 for S6-244. Again, as we said before it is rather unexpected that Mn would be dissolved in natural condition. The five other samples exposed to distilled water do not show Mn in solution. S8-260 and S-246 are showing dissolved Mn (respectively 0.08 and 0.05) after 1 month of exposure at pH 4.8. The two other samples exposed in similar conditions show no Mn dissolved. S8-261 also shows some Mn at pH 5.5, the three other samples subjected to similar conditions show no Mn in solution. Again a much unexpected result as it would mean that under rainwater (pH = 5.5), Mn will be dissolved in natural condition which is clearly not the case as mentioned above. The last outlier sample is S6-241, which also show some Mn at pH 6.4, again unexpected for this pH level.

This study shows that quantifying the changes before and after exposure is challenging as the variations of the methods used here, SEM with EDX, photospectrometry and reflectance spectroscopy are often larger than the changes themselves. The L, a and b colour parameters, derived from the KM photospectrometer and from the ASD spectrometer did not provide a good discrimination between the samples before and after exposure.

In 2007, Lau et al. undertook a study to assess how iron ore hematite powder (a proxy of iron oxide occurring at the surface of the Burrup rocks) reacts to high concentration of pollutants. The iron ore hematite powders were exposed to water, concentrated solvent (benzene, toluene, xylene) or acid/base (1M nitric acid, concentrated nitric acid, 1M sulfuric acid, concentrated sulfuric acid, 1M ammonia and concentrated ammonia) individually in vials for 22 days (both at 25 and 50°C), and then rinsed with water and dried in ambient conditions. The mineralogy, before and after exposure, was characterised with X-ray diffraction and photospectrometry (colour change). The treatment with water did not produce a significant change in colour, nor did exposure to concentrated solvent (benzene, toluene and xylene) or acid/base (1M nitric acid, concentrated nitric acid, 1M sulfuric acid, 1M ammonia and concentrated ammonia) at ambient conditions or at 50°C. However, treatment with concentrated sulfuric acid produced colour change after 22 days in ambient conditions and concentrated sulfuric acid at 50°C caused the material to harden and become white. Most significantly, the sample exposed to concentrated sulfuric acid was transformed to rhomboclase, an iron sulphate.

The conditions of the current study differ from Lau et al. (2007) because (1) instead of iron ore dust, actual natural samples from the Burrup Peninsula/Murujuga were used; (2) no benzene, toluene or xylene was tested; (3) not only Fe was monitored but also Mn, Al, Si, Na and K, (4), the maximal concentrations for sulfuric and nitric acid in the current study were respectively 0.111M and 0.087M and (5) the solutions where the samples were exposed were measured.

Our results show that for gabbros, Fe does not dissolve in the highest concentration of nitric acid (0.0087M) after 3 days or 1-month confirming Lau et al. (2007) results. However, for the granophyres, some Fe occurs for high concentration of nitric acid (0.0087M). Mn and occasionally Al are in solution even for a concentration of 0.001M nitric acid after 1-month. The results of Lau et al. (2007) were also confirmed for sulfuric acid where Fe is in solution at 0.0111M. Mn and Al are also dissolved. The results of Lau et al. (2007) are also confirmed for NH_3, where no Fe dissolution occurs. Using iron oxide dust as a proxy has its advantage as you can undertake X-ray diffraction of the powder, and as such provides an accurate mineralogy before and after exposure but it is limited to Fe dissolution and not the other important elements such as Mn and Al. The current study is a valuable addition to Lau et al. (2007).

Gillett et al. (2012) measured pH from rainwater samples collected at sites 5, 6, 7 and 8 and measured pH values ranging from 4.3 to 7.5. These values, if confirmed, are slightly higher than the pH required for dissolution of the Burrup Peninsula/Murujuga rocks as that this study has presented. However, these values were measured in 2004 and 2005 and might not represent current acidity levels.

Black et al. (2017) measured the pH (>4) of water washings from the Burrup Peninsula/Murujuga rocks in 2003 and 2004 and compared it to the pH (6.8) of weathered rocks collected before industrialisation and kept in “compactus shelves“ at the Western Australian Museum. As these rocks were not subjected to natural conditions, it is difficult to ensure that the pH of 6.8 is representative of what really happens in outdoor settings. However, as it is the case for Gillett et al. (2012), the theoretical pH of more than 4 calculated in Black et al. (2017) are still not low enough (dissolution starts at pH 3.0 to 3.2 based on the results of the current study) to weather the Burrup Peninsula/Murujuga rocks as established by the results of this report.

The precautionary principle should apply here and emission capable of producing pH below 5.5 (the pH of rainwater) should be considered potentially harmful.

9. RECOMMENDATION

In the last 14 years, since the start of the monitoring of the Burrup Peninsula/Murujuga, the volume of industrial activity has increased drastically in particular for iron ore production and liquefied natural gas production and their associated consequences such as port activities, trucks, 4WD, trains and vessels as well as population increase. The two Yara plants for liquid ammonia and ammonium nitrate are also now operational. In addition, public perception and political awareness for the cultural significance of the biggest rock art site in the world has increased significantly. The combination of all these parameters requires a full review and upscale of the monitoring program undertaken in the Burrup Peninsula/Murujuga since 2004. As part of this review, it is recommended that regular measurements of the pH of the weathered surface of gabbros and granophyres in the Burrup Peninsula/Murujuga be conducted as part as a larger monitoring study with more sites and new control sites. Monitoring stations including rain water gauges should be (re) installed on the Burrup Peninsula/Murujuga to measure rainfall amount, pH concentration, cations and anions as well as wet and dry deposition flux of nitrogen and sulphur.

10.REFERENCES

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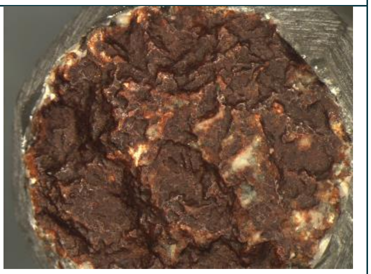
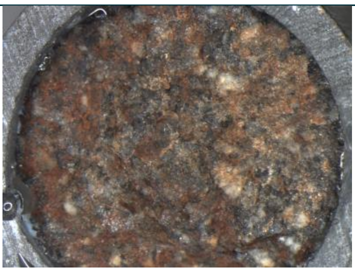
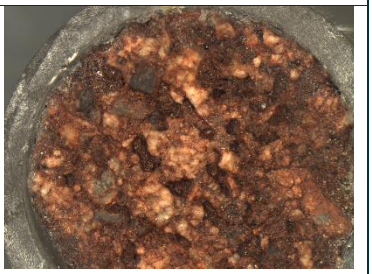
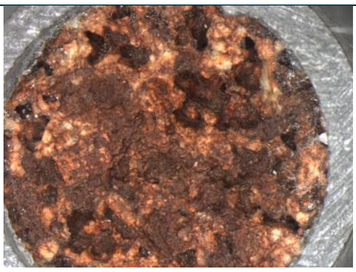
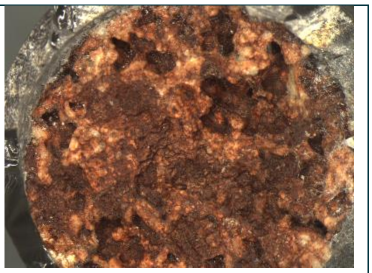
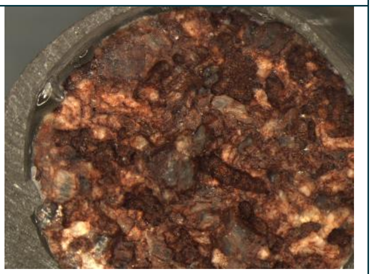
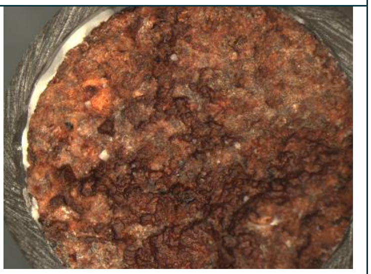
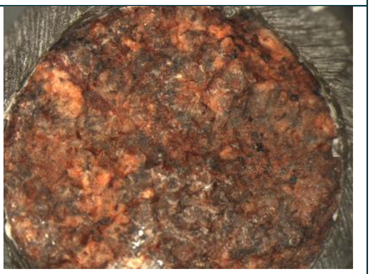
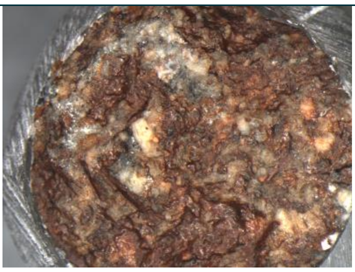
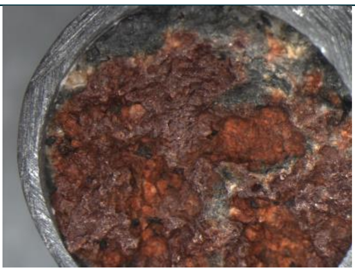
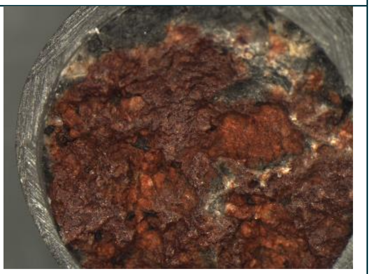
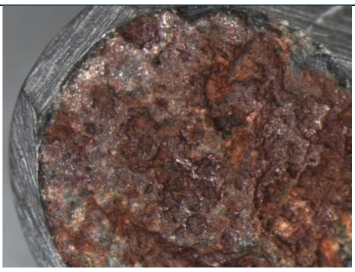
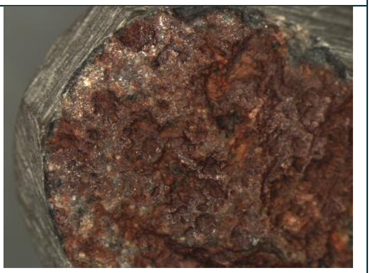
1. Appendix Optical Microscopy Gabbro

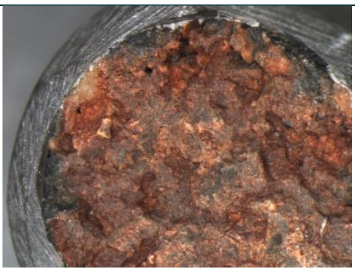
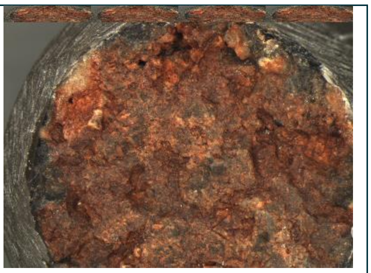
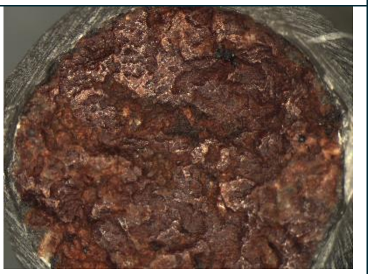
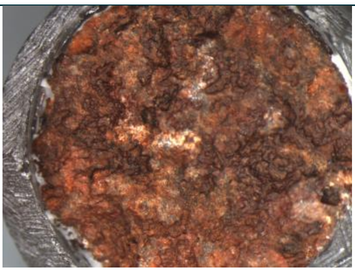
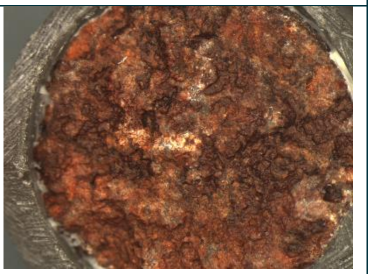
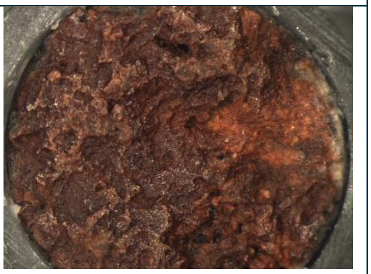
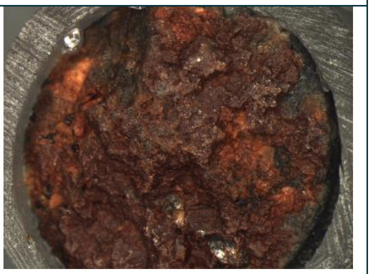
Name	Before	After
S1-2 0.00001 M H_2SO_4		
S1-9 0.001 M NH_4NO_3		
S1-10 0.001 M H_2SO_4		
S1-24 0.0001 M HNO_3		
S1-28 1 M NH_4NO_3		

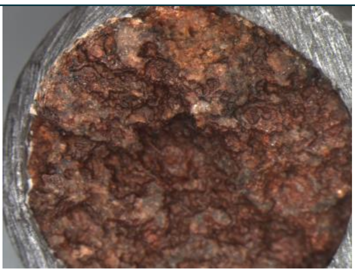
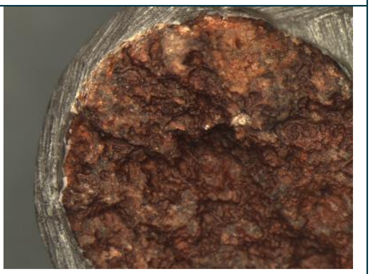
S1-29 H2O		
S1-33 0.00001 M HNO3		
S1-34 0.0001 M H2SO4		
S1-35 0.01 M H2SO4		
S1-47 0.01 M HNO3		
S1-53 0.001 M HNO3		

S7-126 1M NH3		
S7-135 1M NH3		

2. Appendix Optical Microscopy Granophyre

Name	Before	After
S2-83 0.0001 M HNO3		
S2-85 0.001 M NH4NO3		
S2-87 0.001 M H2SO4		
S2-90 1M NH3		
S2-96 0.00001 M HNO3		

S2-97 0.01 M H2SO4		
S2-99 0.0001 M H2SO4		
S4-62 0.01 M HNO3		
S4-67 0.00001 M H2SO4		
S4-69 H2O		
S4-71 0.001M NH3		

S4-76 1 M NH4NO3		
S4-80 0.001 M HNO3		

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