DISSOLUTION RATE OF BASALT

Project submitted to the Central University of Punjab

For the award of

Master of Science

In

Geology

BY

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CERTIFICATE

I declare that the project entitled **“DISSOLUTION RATE OF BASALT”** has been prepared by me under the guidance of Dr. Jitendra Kumar Pattanaik, Assistant Professor, Department of Geography and Geology, School for Environment and Earth Sciences, Central University of Punjab. No part of this project has formed the basis for the award of any degree or fellowship previously.

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CERTIFICATE

This is to certify that the work incorporated in this M.Sc. thesis entitled **"DISSOLUTION RATE OF BASALT"** submitted by Somesh Kumar Panigrahi to the Central University of Punjab in fulfillment of the requirements for the award of the Degree of M.Sc. Geology, under my guidance. I further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma.

Dr. Jitendra Kumar Pattanaik

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Somesh Kumar Panigrahi

ABSTRACT

DISSOLUTION RATE OF BASALT

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Key words: Dissolution, Chipping, density measurement, grinding and sieving, XRD, ICP-MS, time, pH, grain size, temperature, basalt

Physical weathering, Chemical weathering, climate and grain size strongly influences the weathering rate of dissolution. To determine the basalt dissolution rate at various physical-chemical conditions and create an artificial weathering set up by controlling pH, time, grain size in the lab. Three fresh (F.R A1, A2 and Fresh basalt (2/RT12/2)) and one weather (B1) samples of basalt was taken for the defining the rate of weathering. 125-75 and 75-38µm grains size of samples were treated with pH 4, pH 6 continuously agitate for 24, 72, 48 hours and 168 hours at room temperature. Mineral phase identification and geochemical measurements were carried out using XRD and ICP-MS analysis. B1 is less dense compared to other three samples (F.R A1, A2 and Fresh basalt (2/RT12/2)) and A2 shows the high density. Initial pH 4 changed into pH 4.5 and the pH 6 samples changed into pH 7 during dissolution of basalt. In Acidic condition/ low pH the leached elemental concentration is found to be high. Effect of grain size variation in the dissolution rate found to be less. The dissolution rate is higher in the initial stage and reduced with time. Weathered samples shows higher mineral dissolution rate compare to the fresh basalt.

(Name and signature of student) (Name and signature of supervisor)

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Chapter-1
Introduction

1.1. Introduction:

The nutrient production capacity of the geosphere is controlled mainly by weathering rates in addition to the chemical and mineralogical composition of the rock. In the beginning, physical weathering implies the reduction of the size of the particles without changing in the chemical or mineralogical composition of the primary minerals. It is a very important process, since it creates a larger surface area from which the chemical attack in the open is very easy. (http: lawr. ucdavis.edu/classes/ssc219/biogeo/weath.htm)

In the process of chemical weathering, the changes occur in the chemical as well as in the mineralogical composition of the primary and secondary minerals. The chemical weathering rates are influenced mainly by the surface area of the mineral, the temperature, the intensity of the leaching, the mineral composition, the pH and the concentration of chelates. It also formed clay minerals or secondary minerals, which provide many important characteristics to the soil, such as ion exchange and sorption capacity. (http: lawr.ucdavis.edu/classes/ssc219/biogeo/weath.htm)

Weathering rates of minerals are directly proportional to the surface area of mineral, which is exposed to the weathering. It is also believed that the surface coating of the organic matter or iron oxides may impede the relative surface of mineral and they also may hinder the rates of weathering, because the obstruction of transmission of reaction products and reactants by the surface coating.(lawr.ucdavis.edu/classes/ssc219/biogeo/weath.htm)

Climate is also the primary factor which greatly affects the rates of weathering. Relative studies show that the rates of weathering are a linear function of effective precipitation (that is precipitation minus evapo-transpiration), as well as an exponential function of temperature (White and Blum, 1995).

The grain size also influences the rates of weathering. The smaller the grain size the greater will be the surface area for the chemical attack (Bangar, 2013).

Compared to single grains or rocks of homogeneous lithologies (e.g. limestone) the dissolution of basalt is more complex. Minerals which are present within the basalt dissolve at a different rate. There are some minerals which can release more than one divalent metal cation (Ca^{2+}, $Mg^{2+}$and Fe^{2+}).Mg^{2+} and $Fe^{2+}$are the sources which are expected to be the olivine with end member compositions of Mg_2SiO_4 –Fe_2SiO_4 or pyroxene with end member compositions of $Mg_2Si_2O_6$ – $Fe_2Si_2O_6$ – $Ca_2Si_2O_6$. Olivine is a main favorable source of these divalent cations because its dissolution is faster as compared to the pyroxene. However the pyroxene dissolution is not as fast as olivine, all three relevant divalent metal cations can be sourced from this mineral. Ca^{2+} can also be sourced from plagioclase (with end-members compositions of$NaAlSi_3O_8$ – $CaAl_2Si_2O_8$) and the glassy matrix, which can be composed of a variety of cations. But the dissolution rate of plagioclase and the glassy matrix is relatively slow. (Wells et al., 2017)

In laboratory experiments the dissolution rates are frequently expressed per unit mineral surface area while in natural experiments the rates of dissolution are frequently expressed per unit of landscape surface. If the amount of mineral surface area per unit of landscape surface is evaluated then the rates of dissolution in the natural system can be compared to those with the laboratory experiment. (Anbeek, 1993)

Importance of Work:

During the process of weathering the behavior of elements will be different based on the chemical properties. Importance of my study is defining the mineral as well as elemental behavior and also to know the rates of weathering. By doing this analysis understanding elemental behavior during weathering has wide implication ranging from geochemical to pollution studies.

1.2 Review of Previous Work:

There are different geologists who worked on the rates of weathering of different minerals which are given as follows:

1. In the recent studies of the weathering processes shows the interaction between the water and the atmosphere associated with oxide and silicate minerals. It is clearly indicated that the rates of these reactions are strongly dependent on the mineral surface structure and that the kinetic mechanism is

mainly controlled by the formation of surface complexes. (Wollast and Chou, 1992)

2. In this paper the dissolution rates of spheres of two magnesian olivine, two plagioclase, and quartz in tholeiitic basalt have been determined at three super- liquidus temperatures and one-atmosphere pressure. There are considerable differences between the dissolution rates among the minerals, e.g. at 1210°, 12° above the liquidus temperature of the basalt, while the labradorite dissolves at 86 μm/h. and the magnesian olivines dissolves at 9 and 14 μm/h (Donaldson, 1985).
3. The dissolution rates of the major upper mantle minerals olivine, orthopyroxene, clinopyroxene, spinel, and garnet have been determined in an alkali basalt melt at superliquidus temperatures and 5, 12, and 30 kb. At low pressure where olivine is the liquidus phase of the basalt, olivine has a slower dissolution rate than clinopyroxene; however, at higher pressure where clinopyroxene is the liquidus phase, clinopyroxene has a slower dissolution rate than olivine. (Brearley and Scarfe, 1986)
4. Results from recent studies both on feldspars and on Ca-Fe-Mg silicates suggest that during dissolution the rate limiting step is a surface controlled reaction which is resulting consequently in a constant rate of dissolution for each of these minerals. On the other hand, previous studies on Fe-Mg-silicates suggest that the dissolution proceed incongruently with the consequent formation of a residual protective layer of altered composition on the surface of the mineral. As a result so-called parabolic kinetics is found where the rate of dissolution decreases with time due to the growth in thickness of such surface layers. (Schott and Berner, 1985)
5. In this paper White and Brantley (2003), defining the weathering rates between laboratory experiment and field. He explained that difference between the Experimental weathering rates for a specific silicate mineral are commonly two to four orders of magnitude faster than that of the field-derived rates. He concluded that the relative rates at which the silicate minerals weather in the laboratory are sometimes different than the rates which are observed in the field. For example, however plagioclase and K-feldspar have comparable laboratory rates, but the field weathering rate of plagioclase is much more rapid compared to the K-feldspar (White and Brantley, 2003).

6. This paper describes the enstatite dissolution rates which are measured at far from the equilibrium conditions. The dissolution rates were measured as a function of aqueous magnesium as well as silica activity at pH ranging from 1 to 11 and temperature ranging from 28°C to 168°C.All the rates were measured using mixed flow reactors and exhibited the stoichiometric dissolution. Rates present at pH 2 are independent of aqueous silica activity, but decrease with increasing aqueous magnesium activity. All velocities were measured using mixed flow reactors and showed the stoichiometric solution. The speeds present at pH 2 are independent of the aqueous activity of silica, but decrease with increasing magnesium aqueous activity. At constant temperature rates, they continuously decrease with increasing pH over the entire pH range examined (Oelkers & Schott, 2001).
7. To determine the crystalline basalt dissolution rate at pH 4 and 10 and at temperature 25° to 75°C. The dissolution rates are measured using a mixed flow reactor. Here comparison is done between basaltic glass and crystalline basalt, because the materials collected from dyke on Stapafell Mountain on Reykjanes peninsula in Iceland similar to the dissolution rate of basaltic glass as the experiment done by Oelkers and Gislason (2001) and Gislason and Oelkers (2003). Here the comparison between crystalline basalt and basaltic glass suggest that the rate of crystalline material is lower. (Gudbrandsson et al., 2008)

1.3 Research Problem:

In this study the experiment of rate of dissolution of basalt done in the laboratory by controlling pH, temperature, time and grain size. Here we are choosing the basalt because it is having finer grain size, but if we see the other rock types they are having coarser grain size, where mineral wise rate quantification would be required.

The objectives of the study include quantifying:-

a) Variation in the rate of weathering due to grain size difference.
b) Change in rate of weathering at different pH level.
c) Changes with the interaction time i.e. the change in rate of weathering at different time period.
d) How the rate of weathering changes between fresh basalt and weather basalt.

Chapter- 2
Study Area

2.1 Study Area:

The samples were collected from two different Districts of Jharkhand. One is from Teenpahar hill (Sahibganj district) and other is from Haripur village (Dumka district).Both the district is present in the north eastern site of the Jharkhand. The Sahibganj district is surrounded by Pakur district in the south, Godda district and small portion of Bhagalpur of Bihar district in the west, Kathihar district of Bihar in the North and West Bengal in the east. The Dumka district is surrounded by the pakur district in the east, Godda and Banka district in the north, Deoghar and Jamtara district in the west and West Bengal in the south. Trend of the Rajmahal basalt is found in both the area.

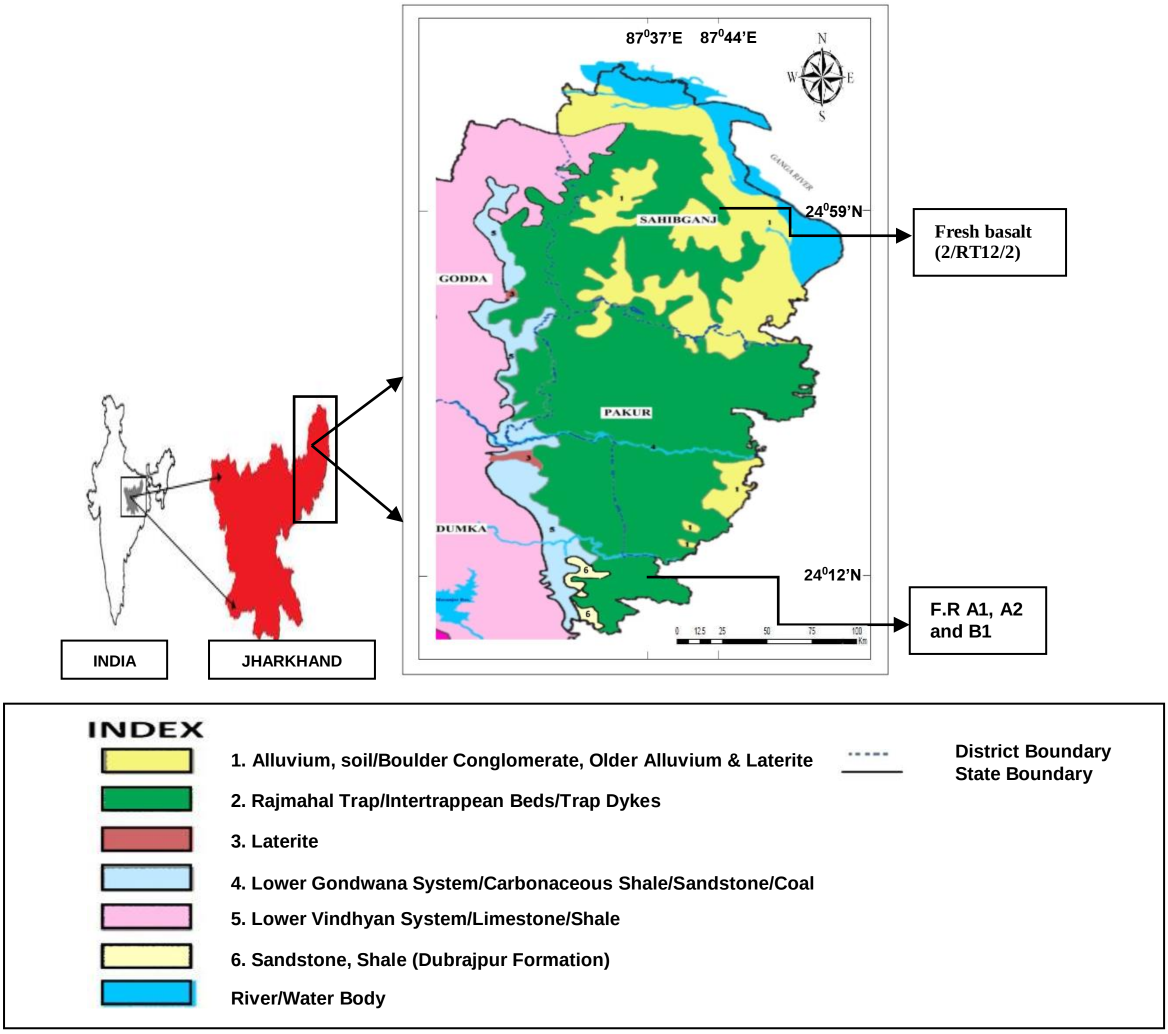


Figure 1. Study area of Sahibganj and Dumka

2.2 Geology:

Rajmahal trap basalt is the major rock type which is found in the Sahibganj district. The other geological formations which are found in this district are alluvium and laterite (Fig. 1). The alluvium which is found in the northern and eastern periphery of the district mainly comprises of sand and sub-ordinate clay. Laterites are mainly of in situ origins, which are formed by the sub-aerial erosion of underlying basalts under the favorable conditions of climate. (CWGB, 2013)

In the Dumka district semi-consolidated rocks of the Barakar Formation of Lower Gondwana Group occurs at the northeastern part. The Rajmahal trap basalts, intertrappean sandstones and shales also found in the northeastern margin of the Dumka district (Singh et al., 2012).

2.2.1. Lithology and Lithostratigraphy:

(1)Dubrajpur Formation: This formation is present between the underlying Barakar and the overlying Rajmahal trap. It contains conglomerate, ferruginous sandstone, coarse pink felspathic sandstone, red and brown siltstone and clay. It occurs as narrow discontinuous bands which is striking the Rajmahal formation along the western margin of the Rajmahal hills. (Mahadevan, 2002)

(2) Rajmahal Formation: This formation lie over the Dubrajpur formation and it overlaps the Barakar onto the crystalline basement along the western margin. The group has a maximum thickness of 330m, but it is thins down to the south near the eastern periphery of the Raniganj basin. The inter-trappean beds of the Rajmahal group contain sandstone, carbonaceous shale, grey shale and tuff. The Rajmahal formation may be divided into four major successive zones such as: (Mahadevan, 2002)

a) Basalt lower trap flows with unfossiliferous intertrappean beds
b) Successive lava flows with highly fossilifeorus intertrappean beds
c) Overlying lava flows with scarcely fossilifeorus intertrappean beds
d) Lava flows with no intertrappean beds

Table 1. Lithostratigraphy of the Rajmahal Formation (simplified from Sengupta, 1988 and Mahadevan, 2002)

Rajmahal Formation	Alluvium Laterite	
	D. Upper trap flows with and without Intertrappeans scarcely fossilifeorus	Cretaceous
	C. Upper trap flows with fossilifeorus intertrappean Bed 8 with Taeniopteris spatulata- Brachyphyllum rhombicum. Assemblage zone 3	Lower Cretaceous
	B. Lower Trap flows (4 to 6) with fossilifeorus intertrappean beds (4 to7) with Cladophlebbis indica-Dictyozamites indicus Assemblage zone 2	Middle Jurassic
	A. Lower Trap flows (1 to 3) with unfossiliferous intertrappean beds (1 and 2)	
……………………………………**Igneous Contact**……………………………		
Dubrajpur Formation	Baked sandstone, siltstone	Lower Jurassic
	Fossiliferous siltstone with Ptylophyllum acutifolium and Gleichenites Gleichenoides. Assembly Zone 1	
	Pebbly sandstone	
	Coarse Sandstone, shale and clay beds	Triassic

2.3 Geomorphology:

Sahibganj district is mainly drained by the Ganges, Gumani and Morang rivers. Except the Ganges River all these rivers are seasonal in nature. During monsoon the Gumani and Morang River contribute to the major surface run-off. However the Dumka district is mainly drained by the Brahmani, the Baslo, and the Mayurakshi rivers with their numerous tributaries. (CWGB, 2013)

2.4 Soil types:

The major soil type found in the Sahibganj district is the Rajmahal type soil which is derived from the basaltic lava. The other soil types which are found in this district are Tal soil, eroded scarp soil, foothill soils, red soil and alluvial soil.

Near the Sahibganj plains the clayey loam type alluvial soil also found. The major soil types of Dumka district are sandy loam to clay loam, non-calcareous and slightly to moderately acidic. (CWGB, 2013)

2.5 Rainfall and Climate:

2.5.1 Rainfall:

The normal average rainfall for the Sahibganj district is ~1575mm, whereas the average annual rainfall for the Dumka district is ~1391.40 mm and the normal annual rainfall is ~1422.5 mm. (CWGB, 2013)

2.5.2 Climate:

Sahibganj district is mainly characterized by the humid to sub-humid climate whereas the Climate of the Dumka district represented by nearly warm and humid climate. In the Sahibganj the maximum temperature reaches upto ~ 44.4^0c in the summer and the temperature falls to ~6.8^0c.However in Dumka the temperature falls to ~ 4^0c during the winter and during summer the temperature rises to ~ 46^0c. (CWGB, 2013)

Chapter- 3
Material and Methods

Sampling and analytical methods:

Rock samples (basalt) from Rajmahal area collected and analysed. The detailed of sampling and techniques which is used are described below.

3.1. Sampling:

There are total 4 samples have been collected from two different profile. Out of 4 samples 3 (F.R A1, A2 and B1) are from one weathering profile (Fig. 2 & 4) and one (Fresh basalt (2/RT12/2)) from other weathering profile (Fig. 3) developed over Rajmahal Basalt. Sample locations are marked in the Google earth image (Fig. 5).

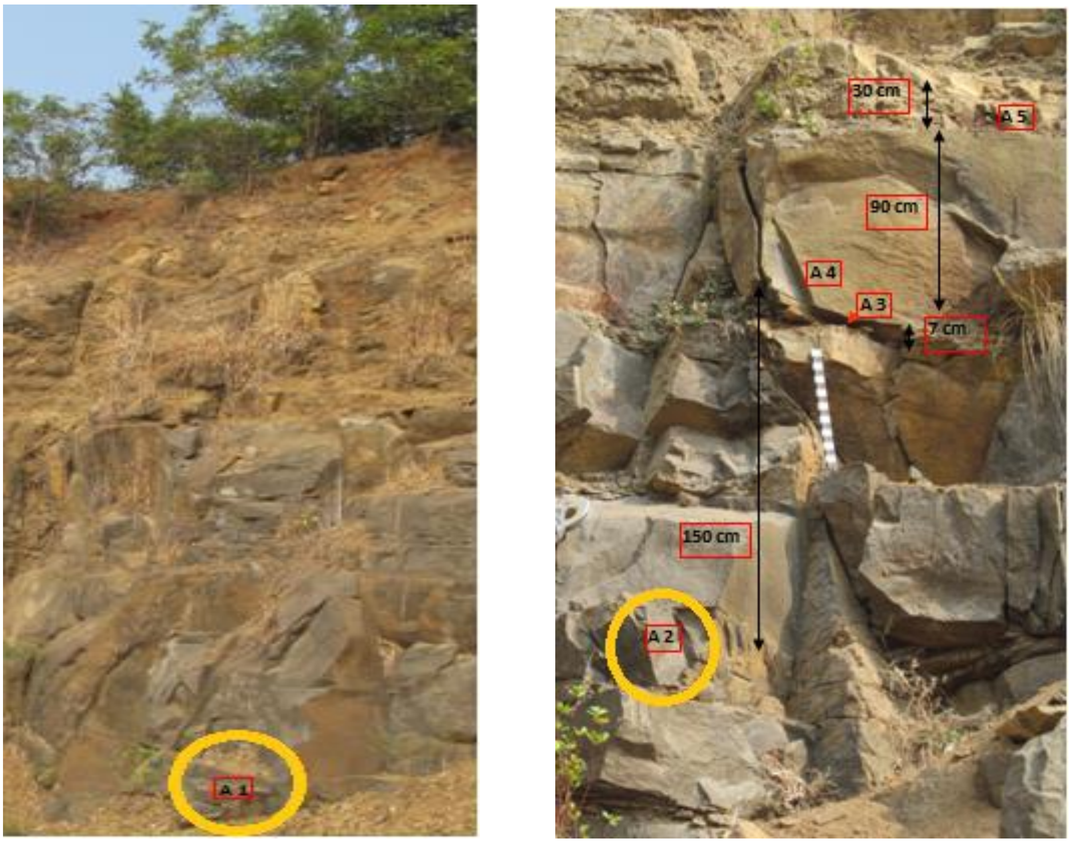


Figure 2. Showing the basalt profile of F.R A1, A2

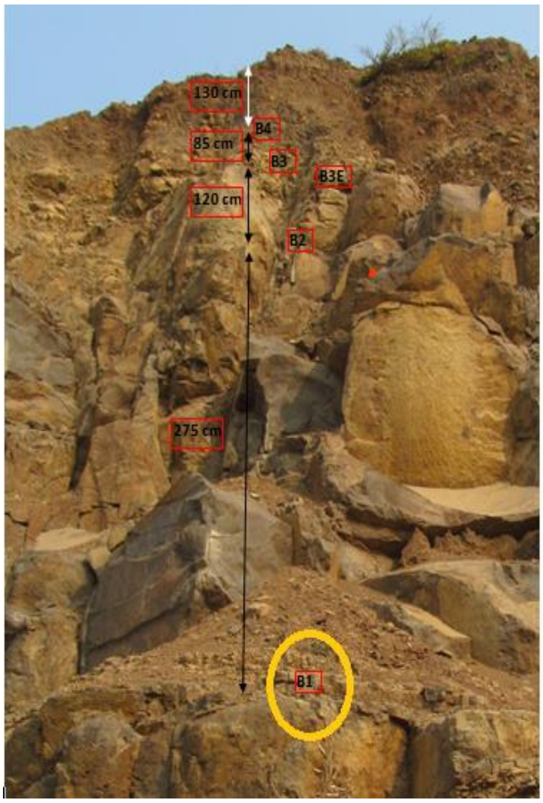


Figure 3. Showing the profile of weathered basalt B1

Figure 4. Showing the profile of Fresh basalt (2/RT12/2)

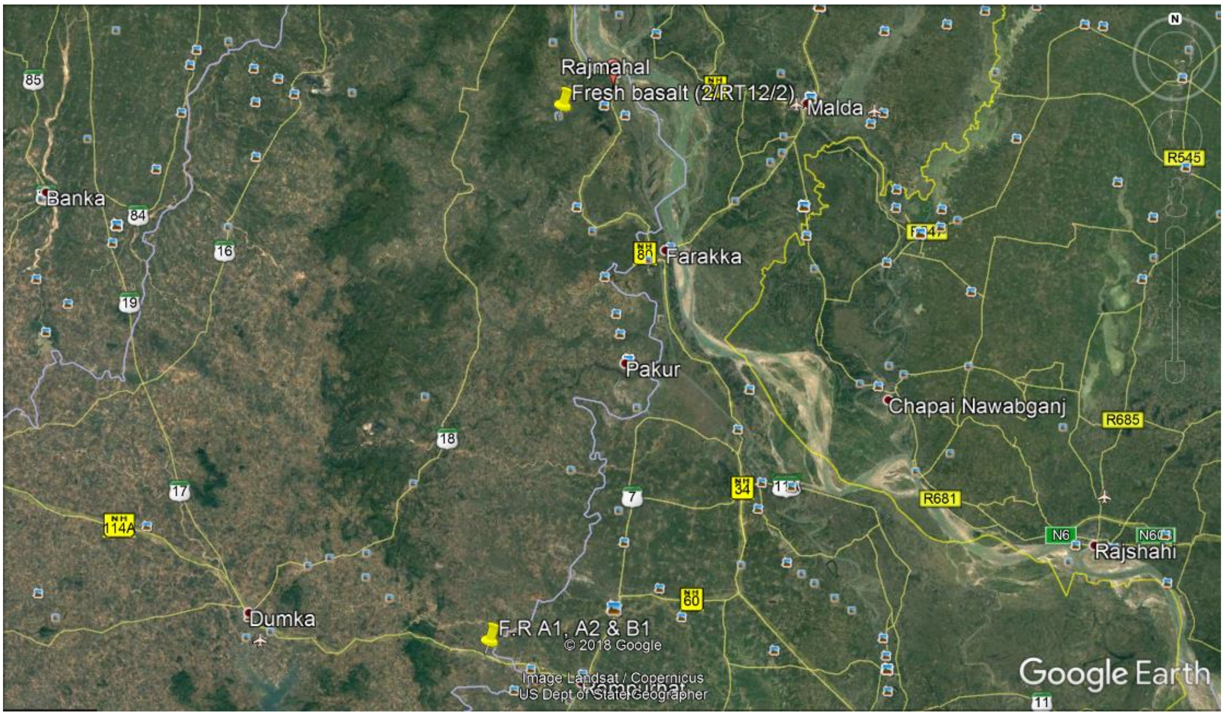


Figure 5. Showing the location of samples in Google earth

Table 2. Location of samples

Sample name	Latitude	Longitude	Altitude
F.R A1	24^0 12’ 37.08” N	87^0 37’ 37.2” E	120m
A2	24^0 12’ 37.08” N	87^0 37’ 37.2” E	120m
B1	24^0 12’ 37.08” N	87^0 37’ 37.2” E	120m
Fresh basalt (2/RT12/2)	24^0 59’ 16.8” N	87^0 44’ 34.8” E	68m

3.2. Analytical methods:

There are different processes involved in this study such as Chipping and density measurement, grinding and sieving, XRD analysis and dissolution of basalt (ICP-MS analysis).

3.2.1 Chipping and Density measurement:

Rock samples were cleaned with tap water followed with deionized water. Samples were dried in the oven at 45^0c and following sample crushing using steel mortar and pestle. Different size fractions were separated using sieve set. Then I kept the chips in a beaker and washed with Elix solution two to three times. Then I did Ultrasonification of the samples at temperature 29° C for 10 minutes. Again I washed the chips with Elix solution. Then I kept the chips in oven at 45° C.

Then I took three chips from each sample. Then I took weight of chips (three chips together) and small beaker (three beakers for one sample) using the weighing machine (Metlor Toledo) in the Plant Science Lab (Fig.6). Then I took a centrifuge tube and added Milli Q solution up to 9ml and clear the bubbles from the centrifuge tube, added single chips with the help of plastic scissor. After adding the chips the solution rises above, pipettes the excess solution and added the pipetting solution into small beaker. I did three times for three chips for one sample. Then I took the weight of those beakers together in the Plant Science Lab. After getting the weight of beaker I subtracted the weight of the volume of water displaced from weight of the bottle to get the displaced volume. Then I divided the weight of the chips to the displaced volume to get the density. It was same for other two samples (fresh samples). But in case of weather samples it was slightly different. Chips were wrapped before added into the centrifuge tube. Then displaced volumes of wrapped chips were calculated. Then I calculated the density and displaced volume of parafilm. After that I calculated the displaced volume of chips by subtracting displaced volume of parafilm from displaced volume of wrapped chips. Then I got the density by dividing mass and volume of the chips.

Figure 6. Photograph of weighing machine Metlor Toledo

3.2.2 Grinding and Sieving:

I grinded the chips by using Tungsten carbide in the grinding machine for ten second intervals in the lab of Geography and Geology (Fig. 7) and sieved the grinded samples using the sieve size of 4.75, 2, 1 in mm and 500, 250, 125, 75, 38µm by hand . After sieving I again grinded the samples for ten second, I did this until the amount of samples (4.75 mm) less. Then I used 7 beakers and one plastic rod for washing the grinded samples of different size fractions with Milli Q solution to remove the impurities of tungsten carbide. After cleaning the samples I kept each samples in seven petridish. Then I kept the petridish in the ovan at 45^0c for drying the samples. Grinding process was same for other two samples (fresh samples). As weather basalt samples were soft I grinded the samples with the help of small mortar and pestle. Then I crushed the samples and sieved until the amount of samples less. Then washed with Milli Q and kept in the ovan at 45^0c.

Figure 7. Photograph of the grinding machine (Retsch RS200)

3.2.3 XRD analysis:

X-ray powder diffraction (XRD) is mainly used for identifying the mineral phases present in the rock, sediments or any solids. It also used for the identifying different crystalline materials. This technique is now mainly used for the study of the different crystal structures as well as atomic spacing. Now a day, it is a faster tool for geo-researcher to identifying minerals.

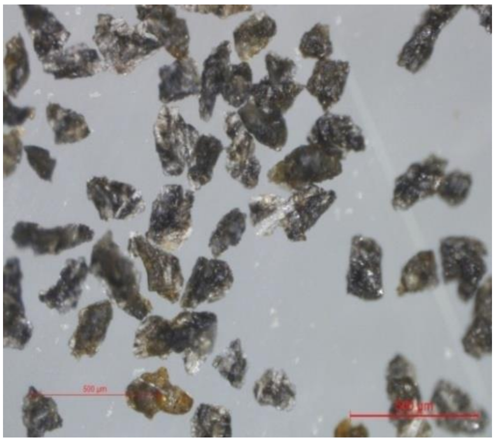
During the process from the cathode ray tube the X rays are generated and then these rays are filtered to produce the monochromatic radiation, then it collimated and directed towards the samples. Then a detector detected the X-ray signal electronically or by micro processor which converted the signal to count rate. This principle is on the basis of Bragg's law ($n\lambda=2d \sin \theta$) where n is the integer, λ is the wavelength of X-ray, d is spacing between the interplanar spacing between the crystal and θ is the angle of incidence X-rays beam. (Flohr, 1997)

Figure 8. Photograph of the X-Ray Powder diffraction facility (PANalytical) at IUAC, New Delhi

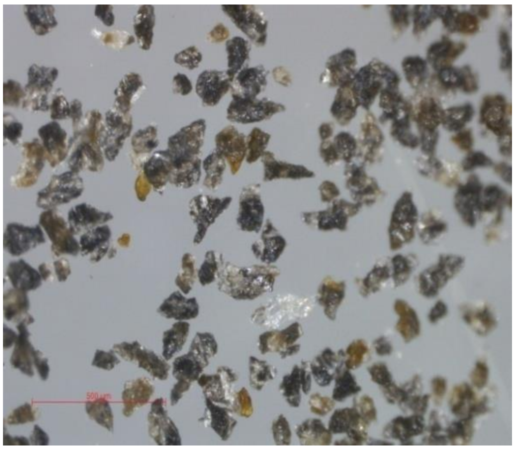
The samples were sent to the Inter University Accelerator Centre (IUAC), New Delhi for XRD analysis. The XRD analysis is done with the PANalytical machine (Fig 8). After getting the result we analysed the XRD data using X pert High score. The XRD data are in .Xrdml format. Here we mainly select the minerals according to peak. For selecting the mineral we have to avoid the minerals which are synthetic and which have RIR value zero, extreme RIR values.

3.3. Dissolution of basalt:

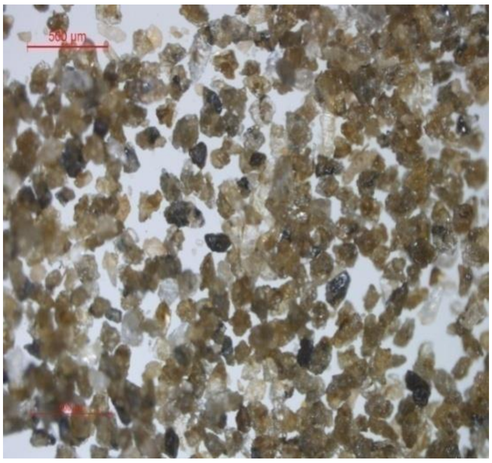
For doing this analysis we have to take two grain size i.e. 125-75 µm and75-38 µm of each samples and took time of 24, 48 and 72 hours and 168 hours. Before doing this analysis I properly checked the samples in the microscope to see whether grains are clean, no fine particles are attached to the surface of the grain and grains are mono minerallic or poly mineralic grain (Fig 9). Then we have to take 1 gram for each sample. I took the weight of the samples using the weighing machine (Metlor Toledo) of Plant Science lab (Fig 6). I took total 28 samples for this experiment and used 28 centrifuge tubes. I used pH 4 and 6 and making two different solutions. For making pH 6 I made the solution using Mill Q solution and for making pH 4 I added approximately 300 ml Milli Q with 0.3 HCl and also took two 10 ml (pH 4 and 6) solution of blank sample. I took 10 ml solution for each 1 gram samples. I added this solution using pipette of 5 ml. Then I shake the samples using stirrer in the lab of Geography and Geology (Fig 10). Then the samples were filtered to a small bottle and then the samples were goes for the ICP-MS test.



(a)



(b)



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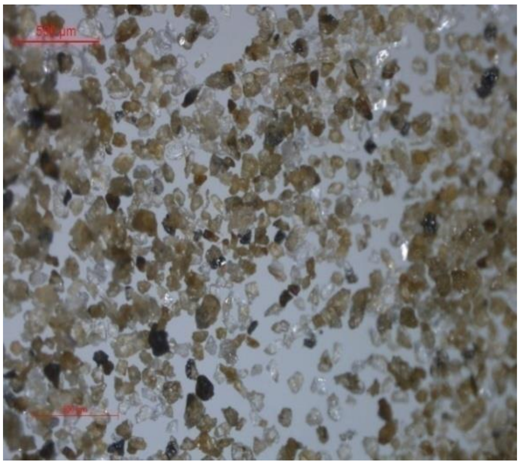
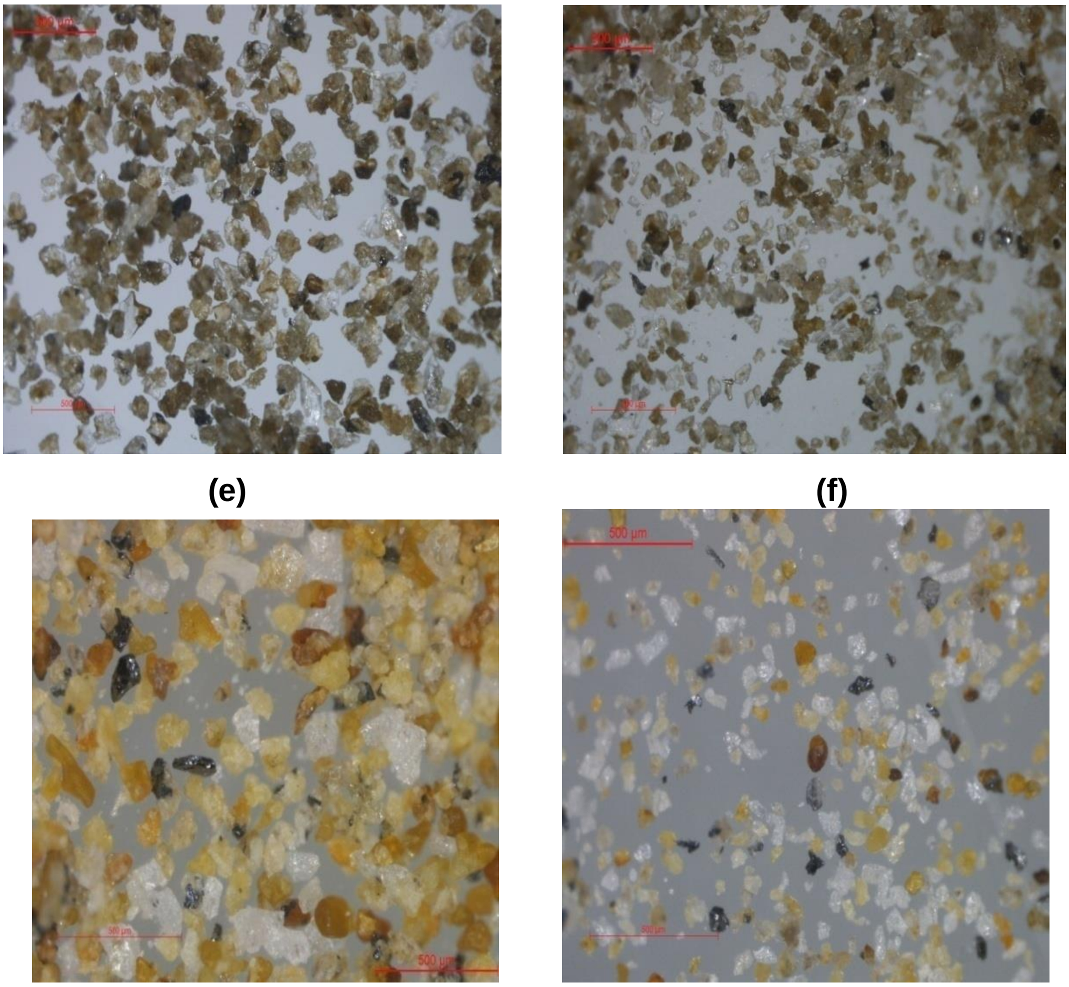


(d)



(e) (f)

(g) (h)

Figure 9. Image of different grain size of basalt (a) Fresh basalt(2/RT12/2)-125-75 µm, (b) Fresh basalt(2/RT12/2)-75-38 µm, (c) F.R A1-125-75 µm, (d) F.R A1- 75-38 µm, (e) A2-125-75 µm, (f) A2-75-38 µm, (g) B1-125-75 µm, (h) B1-75-38 µm

Figure 10. Stirrer used for continuous agitation of samples

3.4. ICP-MS analysis:

It stands for Inductively coupled plasma Mass Spectrometry. It is mainly used for elemental determination as well as geochemical analysis such as REE (Rare Earth Elements). (Wolf, 2005)

Chapter- 4
Result and Discussion

4.1. Density measurement:

Sample B1 shows the density 1.45g/cm^3 which is less compared to F.R A1, A2 and Fresh basalt (2/RT12/2) (Table 3.). Out of these samples A2 shows the higher density i.e.3.06g/cm^3 while F.R A1 and Fresh basalt (2/RT12/2) shows the density 2.90 and 2.76g/cm^3 respectively.

Here B1 shows the less density value because it is a weather and very smooth sample, but the other samples they show a good density value as they are fresh and compact compared to the B1.

Table 3. Density determination by volume displacement method

Sample No	Chip weight(g)	Volume displaced(g)	Density(g/cm^3)
F.R A1	3.393	1.17	2.90
A2	3.902	1.274	3.06
Fresh basalt(2/RT12/2)	2.817	1.02	2.76
B1	2.857	1.974	1.45

4.2. Weight of the samples:

The final weight of different size fraction of samples taken for analysis is listed in the Table 4.

Table 4. Weight of grinded and sieved samples

Sample Name	Grain Size								
	4.75mm	4.75-2mm	2-1mm	1-500µm	500-250µm	250-125µm	125-75µm	75-38µm	<38µm
F.R A1	66g	51g	29g	7g	22g	18g	8g	20g	29g
A2	78g	62g	30g	16g	15g	8g	4g	7g	9g
Fresh basalt (2/RT12/2)	50g	60g	33g	18g	14g	8g	3g	2g	2g
B1	22g	46g	26g	8g	5g	3g	0.69g	1g	2g

4.3 XRD Result:

By doing the XRD data analysis in the X-pert High score we get the minerals like Labradorite, Bytownite, Enstatite, Augite, Olivine, Magnetite, Quartz in the

Fresh basalt (2/RT12/2), F.R A1, A2. In B1 sample we got Kaolinite associated with above minerals found in Fresh Basalt (2/RT12/2), F.R A1 and A2 in Table 5.

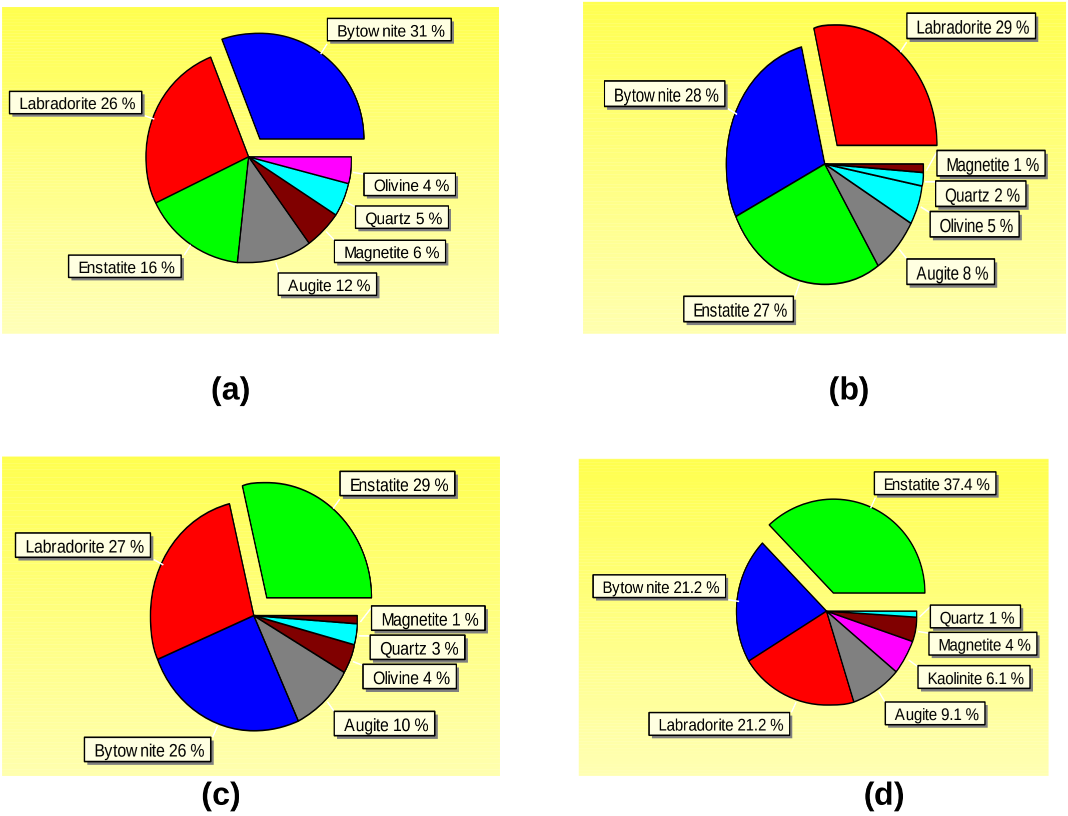
In Figure 11 the semi-quantification percentage of minerals presented in pie chart. Here the Na and Ca rich plagioclase, pyroxene play as major percentage because the samples of basalt are from Rajmahal trap which is enriched with plagioclase, pyroxene. Other than this olivine, magnetite, quartz also found in some minor quantity.

In Figure 12 the different minerals showing the different peaks according to their 2 theta values. The Labradorite present at the 27.805, Bytwonite at 27.881, Enstatite at 27.846, Augite at 29.767, Olivine at 36.524, Magnetite at 35.444 and Quartz at 26.431.

In Figure 13 the comparison between the Fresh Basalt (2/RT12/2), F.R A1, A2 and B1. In three fresh samples the plagioclase percentage is high, but in weather samples the Plagioclase percentage is less. In weather samples less amount of plagioclase found because due to weathering it is moving towards the formation of kaolinite.

Table 5. Semi quantification percentage of Fresh basalt (2/RT12/2), F.R A1, A2 and B1

Sample Name	Labradorite	Bytownite	Enstatite	Augite	Olivine	Magnetite	Quartz	Kaolinite
Fresh basalt (2/RT12/2)	27	32	17	13	4	6	5	-
F.R A1	31	29	29	8	5	1	2	-
A2	28	27	30	10	4	1	4	-
B1	21	21	37	9	-	4	1	6



(a) **(b)**

(c) **(d)**

Figure 11. Pie chart shows the semi quantification percentage of (a) Fresh basalt (2/RT12/2), (b) F.R A1, (c) A2 and (d) B1

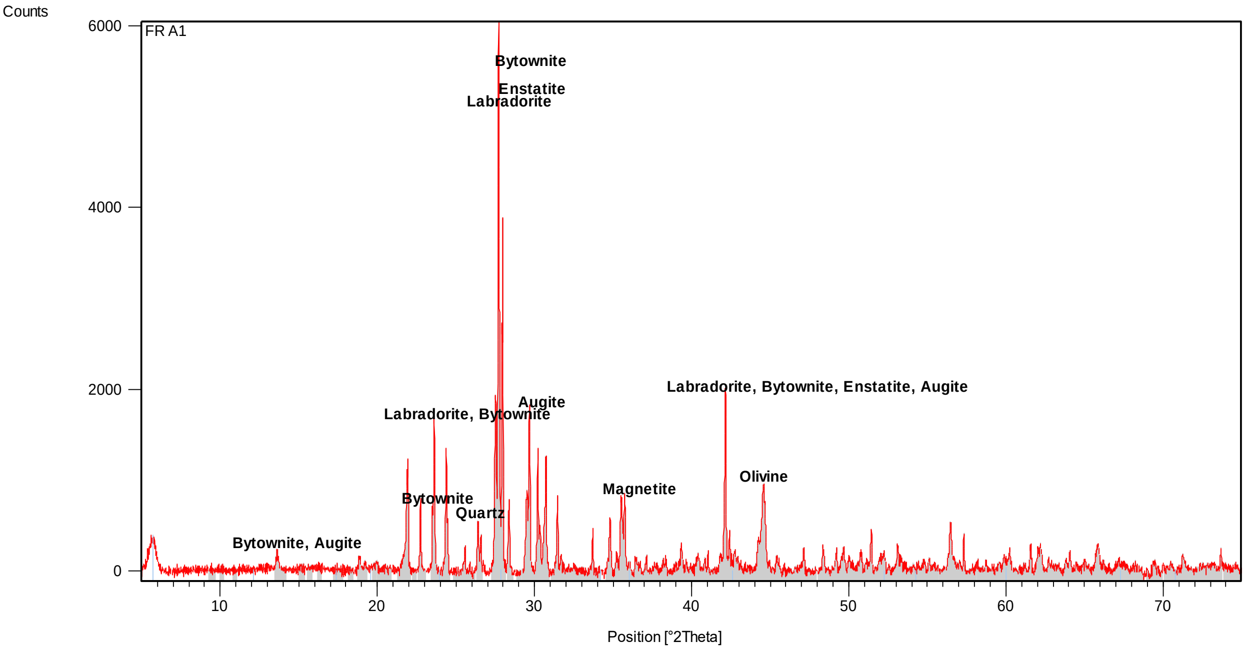


Figure 12. Typical XRD spectrum with selected mineral name and its 2 Theta value.

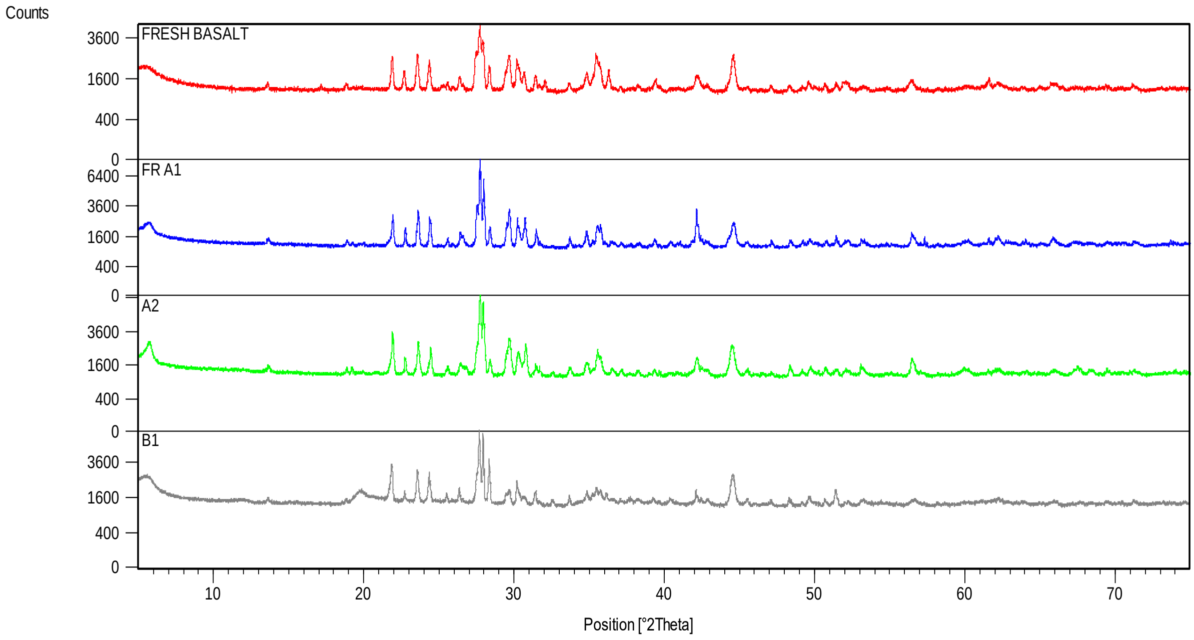


Figure 13. Comparison of XRD spectrum between Fresh basalt (2/RT12/2), F.R A1, A2 and B1

4.4 ICP-MS Result:

Table 6 shows the final pH of 30 samples (including two blank samples of pH 4 and pH 6) of two different size fraction (75-38 and 125-75µm) after keeping the samples of time 24, 48, 72 and 168 hours with continuous agitation by Strrier. After undergoes continuous agitation all the pH 4 samples changed to pH 4.5 while all the pH 6 samples changed to pH 7. But there is no changes occur in case of blank samples.

The observation of elemental concentration variation in this experiment is based on the pH, grain size, time and fresh Vs. Weathered rock. The interpretation is taken based on three cases such as: (a) same sample, grain size, time and different pH, (b) same sample, pH, time and different grain size, (c) same grain size, pH, time and different sample. The total experiment is done only for a maximum time period of 1 week. To overcome this limitation, the interpretation is done only based on elements which can easily react and get removed from the rock. For example Sr which is an easily leachable element.

Table 6. Initial and Final pH of samples after continuous agitation of 24, 48, 72 and 168 hours

Sample Name	Grain size(μ)	Time(hrs)	Initial pH	Final pH
F.R A1	75-38	24 hrs	4	4.5
F.R A1	75-38	24 hrs	6	7
F.R A1	75-38	48 hrs	4	4.5
F.R A1	75-38	48 hrs	6	7
F.R A1	75-38	72 hrs	4	4.5
F.R A1	75-38	72 hrs	6	7
F.R A1	75-38	168 hrs	4	4.5
F.R A1	75-38	168 hrs	6	7
F.R A1	125-75	24 hrs	4	4.5
F.R A1	125-75	48 hrs	6	7
F.R A1	125-75	48 hrs	4	4.5
F.R A1	125-75	72 hrs	4	4.5
F.R A1	125-75	72 hrs	6	7
F.R A1	125-75	168 hrs	4	4.5
F.R A1	125-75	168 hrs	6	7
A2	75-38	48 hrs	4	4.5
A2	75-38	48 hrs	6	7
A2	75-38	72 hrs	4	4.5
A2	75-38	72 hrs	6	7
A2	75-38	168 hrs	4	4.5
A2	75-38	168 hrs	6	7
A2	125-75	72 hrs	4	4.5
A2	125-75	168 hrs	6	7
A2	125-75	168 hrs	4	4.5
B1	75-38	168 hrs	4	4.5
Fresh basalt (2/RT12/2)	75-38	168 hrs	4	4.5
Fresh basalt (2/RT12/2)	125-75	168 hrs	4	4.5
Fresh basalt (2/RT12/2)	125-75	168 hrs	6	7
Blank	-	168 hrs	4	4
Blank	-	168hrs	6	6

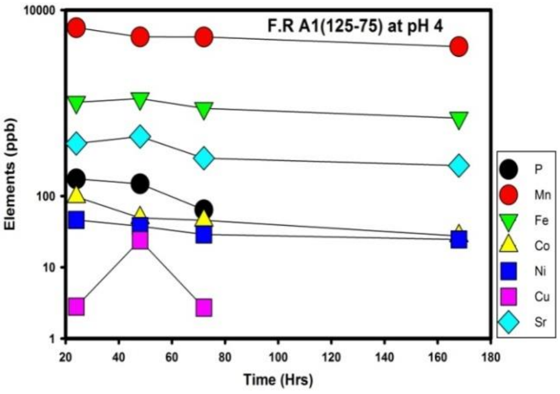
Table 7. Elemental concentration (ppb) in different samples at different pH

Sample Name	Mg	Al	P	K	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Tl	Pb	Th	U
Fresh basalt-125-75µm-1 week-pH 6	10859.9	2348.6	54.2	bdl	50.6	7419.4	9.4	6.6	20.0	10.1	2.2	58.1	bdl	bdl	0.2	6.7	0.2	0.6
Fresh basalt-125-75µm-1 week-pH 6	12053.5	2632.8	93.8	bdl	61.1	8202.1	13.8	9.0	29.2	39.8	0.1	71.2	bdl	bdl	bdl	6.6	bdl	bdl
Fresh basalt-125-75 µm-1 week-pH 4	bdl	bdl	bdl	9792.9	1299.9	3897.7	114.0	434.8	bdl	161.3	5.4	552.5	bdl	bdl	bdl	bdl	bdl	bdl
Fresh basalt-75-38 µm-1 week-pH 4	bdl	bdl	bdl	5450.5	1263.4	3373.0	150.6	337.4	bdl	208.2	4.6	494.4	bdl	bdl	bdl	bdl	bdl	bdl
F.R A1-125-75 µm-1 week-pH 6	bdl	119.5	bdl	4748.8	291.7	829.3	11.8	13.7	38.7	bdl	8.7	210.1	8.0	27.2	7.7	7.8	7.7	12.2
F.R A1-125-75 µm-72 hours-pH 6	bdl	5369.4	187.2	bdl	398.2	bdl	15.1	21.9	38.6	bdl	0.7	278.3	bdl	1.3	bdl	14.2	0.4	1.8
F.R A1- 125-75 µm-48 hours- pH 6	bdl	5235.7	251.3	bdl	607.7	bdl	18.9	36.3	81.2	bdl	0.4	480.3	bdl	35.8	bdl	16.1	0.4	0.5
F.R A1-125-75 µm-1 week-pH 4	bdl	bdl	bdl	7159.8	6560.9	2878.5	27.5	24.6	bdl	174.7	3.7	1666.5	bdl	bdl	bdl	bdl	bdl	bdl
F.R A1-125-75 µm-72 hours-pH 4	bdl	bdl	64.3	4938.0	7332.2	3222.5	45.7	29.0	2.7	bdl	3.9	1813.8	bdl	bdl	bdl	bdl	bdl	bdl
F.R A1- 125-75 µm-48 hours- pH 4	bdl	bdl	148.7	bdl	7339.7	3607.1	49.4	37.8	24.0	bdl	5.4	2329.4	bdl	21.9	bdl	bdl	bdl	bdl
F.R A1- 125-75 µm-24 hours- pH 4	bdl	bdl	174.8	bdl	8161.2	3455.8	97.8	46.3	2.8	bdl	4.6	2150.6	bdl	bdl	bdl	bdl	bdl	bdl
F.R A1- 75-38 µm-1 week-pH 6	bdl	7552.1	181.1	bdl	618.2	bdl	48.5	27.3	96.5	74.6	bdl	265.4	bdl	4.0	bdl	19.3	0.6	1.2
F.R A1- 75-38 µm-72 hours- pH 6	bdl	4253.1	320.9	bdl	419.0	bdl	31.2	19.3	45.7	bdl	0.2	304.0	bdl	bdl	bdl	15.8	0.5	0.4
F.R A1-75-38 µm-48 hours- pH 6	bdl	5968.7	345.7	5945.3	496.6	bdl	44.6	32.3	74.9	41.4	1.2	452.4	bdl	21.3	bdl	20.7	0.9	2.1
F.R A1- 75-38 µm-24 hours- pH 6	bdl	1895.8	219.1	bdl	206.5	7087.7	13.3	29.0	59.7	bdl	0.4	455.6	bdl	20.2	bdl	7.6	0.3	2.8

Table 8. Elemental concentration (ppb) in different samples at different pH

Sample Name	Mg	Al	P	K	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Tl	Pb	Th	U
F.R A1- 75-38 µm-1 week-pH 4	bdl	bdl	bdl	3859.4	4875.2	3287.6	38.6	18.7	bdl	bdl	4.2	1769.7	bdl	bdl	bdl	bdl	bdl	bdl
F.R A1- 75-38 µm-1 week-pH 4	bdl	bdl	1.5	5771.2	5287.8	3326.0	51.7	22.2	bdl	41.4	5.6	1897.6	bdl	bdl	bdl	bdl	bdl	bdl
F.R A1- 75-38 µm-72 hours- pH 4	bdl	bdl	87.9	4386.1	5578.6	3076.4	81.0	27.2	0.3	bdl	4.0	1787.8	bdl	bdl	bdl	bdl	bdl	bdl
F.R A1-75-38 µm-48 hours- pH 4	bdl	bdl	225.4	9506.4	5131.3	3123.0	84.5	27.7	21.3	bdl	4.5	1896.9	bdl	55.8	bdl	bdl	bdl	bdl
F.R A1-75-38 µm-24 hours- pH 4	bdl	bdl	133.9	bdl	6330.3	3612.3	129.6	44.6	6.5	bdl	4.5	2070.0	bdl	bdl	bdl	bdl	bdl	bdl
A2-125-75 µm-1week-pH 6	bdl	2384.8	79.3	bdl	146.2	8902.2	7.1	8.0	16.3	bdl	0.9	278.0	bdl	bdl	bdl	2.8	0.4	2.3
A2-125-75 µm-1week-pH 4	bdl	bdl	bdl	2275.4	4068.8	3887.0	141.1	119.4	bdl	501.6	3.4	2211.3	bdl	bdl	bdl	bdl	bdl	bdl
A2- 125-75 µm-72 hours- pH 4	bdl	bdl	111.3	bdl	6065.7	5008.8	355.7	177.5	46.1	986.0	7.3	3388.2	0.1	76.8	bdl	bdl	bdl	bdl
A2-75-38 µm-1week-pH 6	bdl	344.6	bdl	bdl	60.2	405.0	2.2	0.2	1.5	bdl	0.3	265.9	bdl	bdl	bdl	bdl	bdl	0.6
A2- 75-38 µm-72 hours- pH 6	bdl	1403.2	246.7	bdl	75.7	2909.5	4.9	5.4	3.6	bdl	0.6	395.3	bdl	20.1	bdl	3.2	bdl	0.8
A2- 75-38 µm-48 hours- pH 6	bdl	1797.6	350.5	bdl	100.1	4648.7	10.5	11.4	57.6	34.2	0.8	531.1	bdl	34.5	bdl	3.0	0.1	1.4
A2-75-38 µm-1week-pH 4	bdl	bdl	bdl	4553.0	5122.7	3401.4	457.8	140.4	bdl	2650.9	3.1	2150.3	bdl	bdl	bdl	bdl	bdl	bdl
A2- 75-38 µm-72 hours- pH 4	bdl	bdl	86.2	828.2	5709.9	3626.1	770.4	150.1	bdl	3095.8	5.2	2589.9	bdl	bdl	bdl	bdl	bdl	bdl
A2- 75-38 µm-72 hours- pH 4	bdl	bdl	46.1	bdl	4934.4	3168.8	651.9	127.5	bdl	2651.6	4.3	2247.3	bdl	bdl	bdl	bdl	bdl	bdl
A2- 75-38 µm-48 hours- pH 4	bdl	bdl	195.9	bdl	5471.3	4433.4	664.8	157.1	62.2	4516.6	7.0	2968.3	0.1	49.5	bdl	bdl	bdl	bdl
B1-75-38 µm-1week-pH 4	bdl	bdl	89.0	6140.6	853.1	3568.4	8.3	17.6	bdl	143.7	4.2	2561.3	bdl	88.4	bdl	bdl	bdl	bdl

4.4.1 Comparison of elemental concentration sample, grain size, time and different pH:



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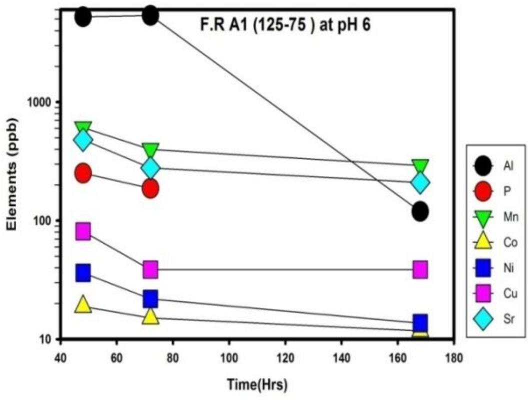

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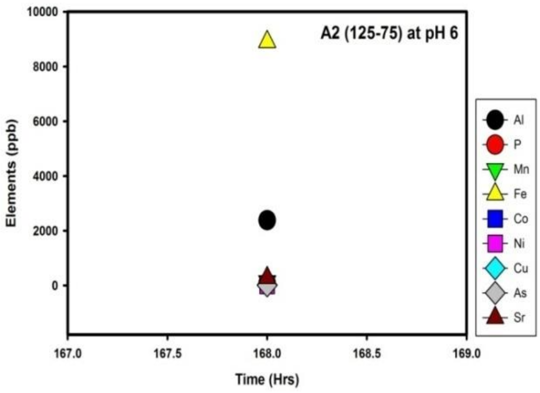

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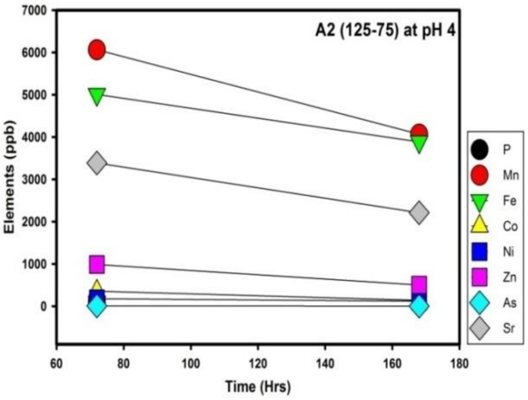

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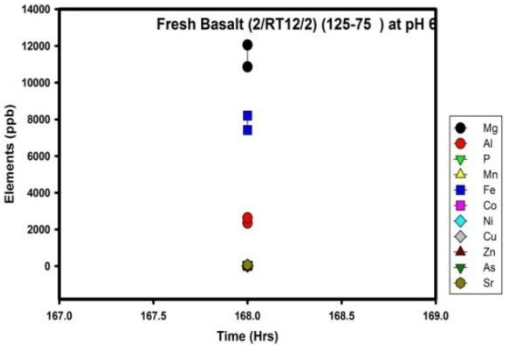

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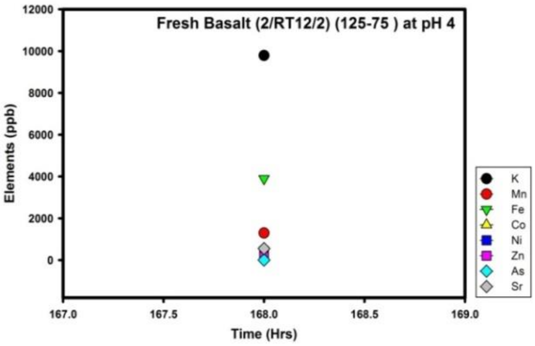

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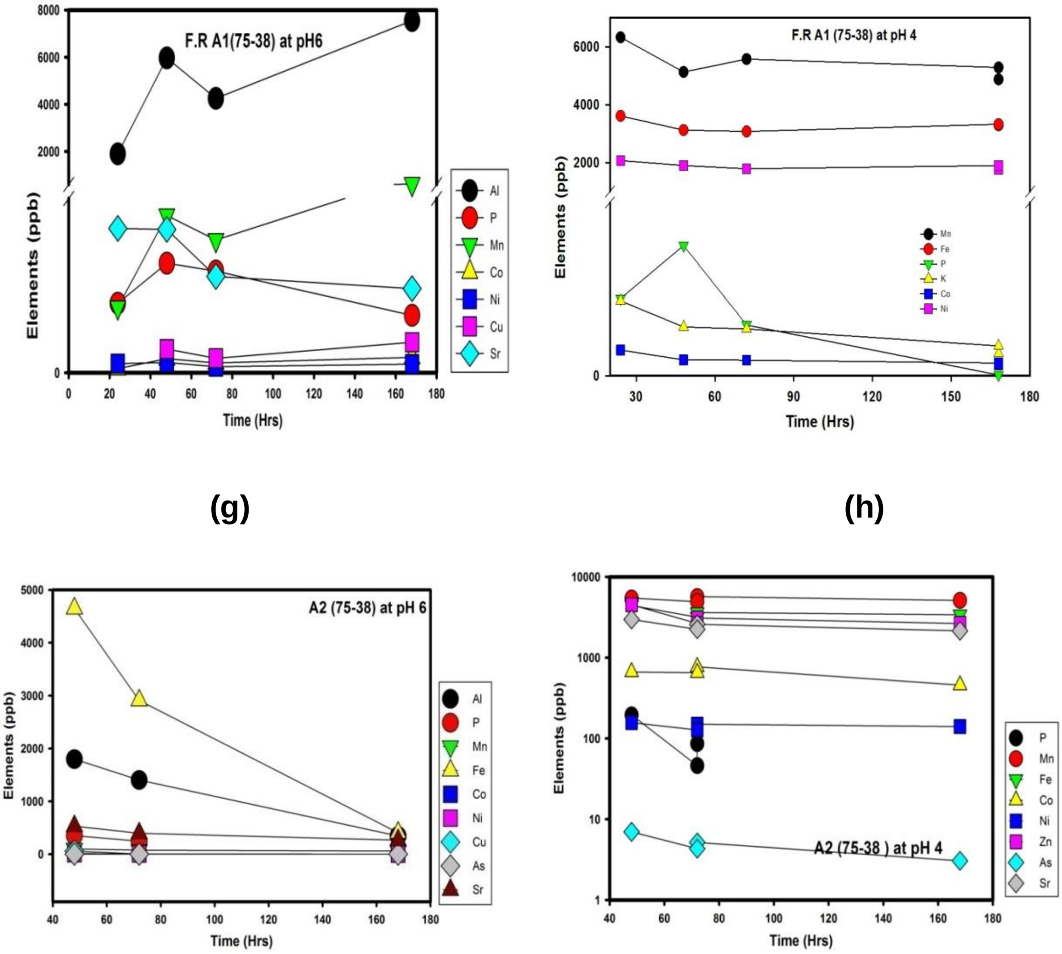
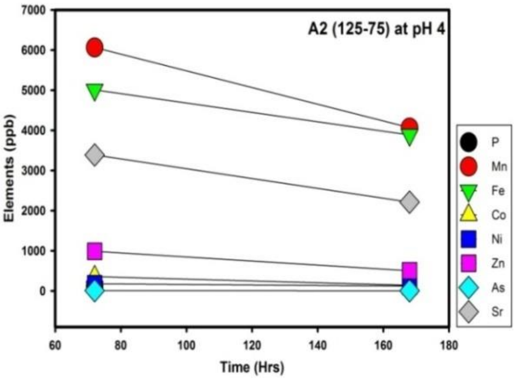


(g) (h)

(i) (j)

Figure 14. Plot shows elemental concentration (a) F.R A1 (125-75µm) for pH6, (b) F.R A1 (125-75µm) for pH 4, (c) A2 (125-75µm) for pH6, (d) A2 (125-75µm) for pH4, (e) Fresh Basalt (2/RT12/2) (125-75µm) at pH6, (f) Fresh Basalt (2/RT12/2) (125-75µm) for pH4, (g) F.R A1 (75-38 µm) for pH6, (h) F.R A1 (75-38µm) for pH4, (i) A2 (75-38 µm) for pH6 and (j) A2 (75-38 µm) for pH4.

4.4.2 Comparison of elemental concentration among same sample, pH, time and different grain size:



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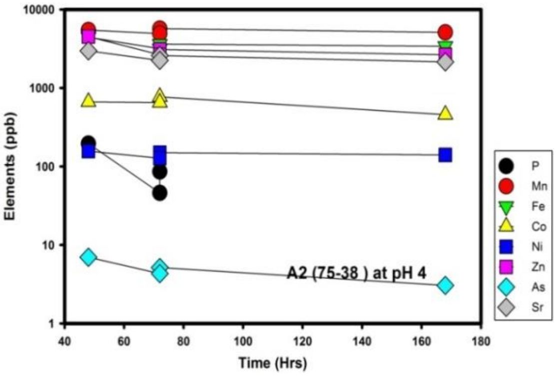

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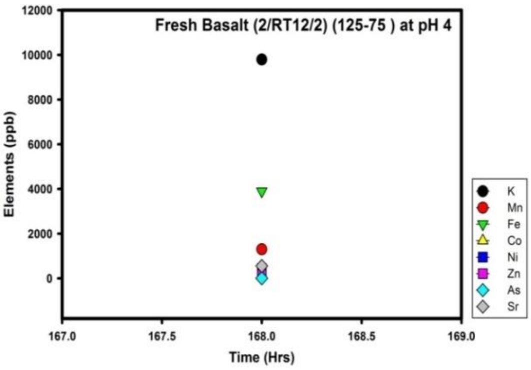

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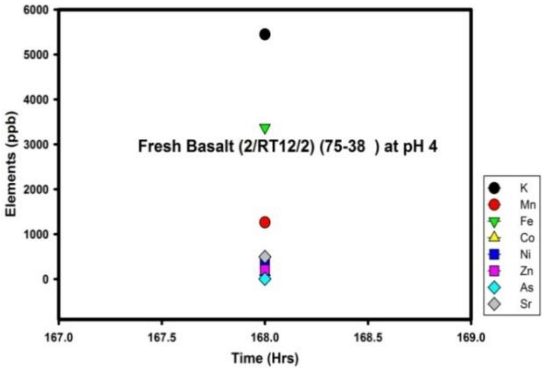

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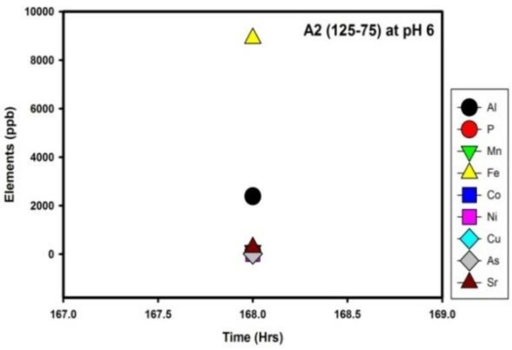

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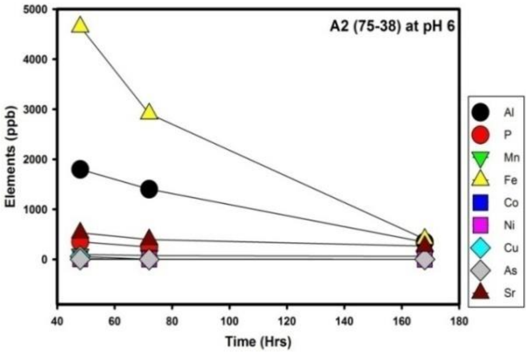

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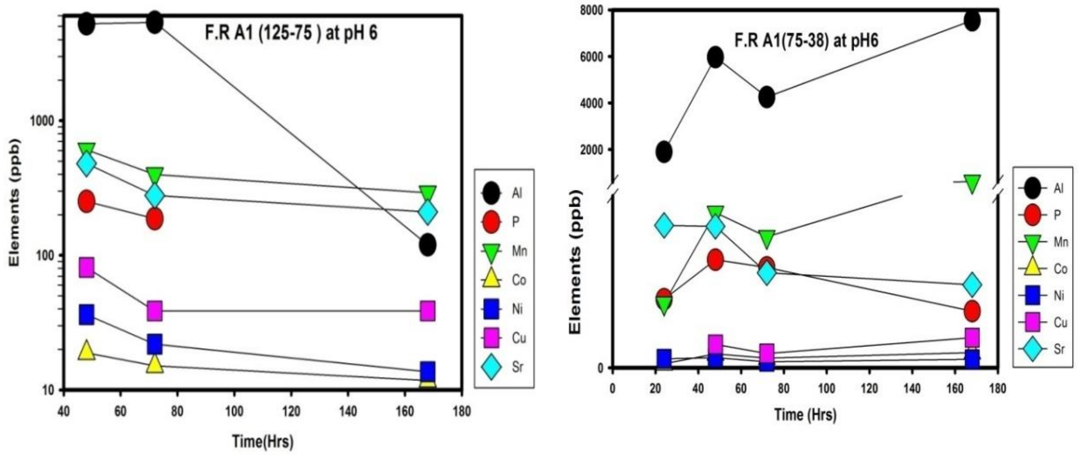
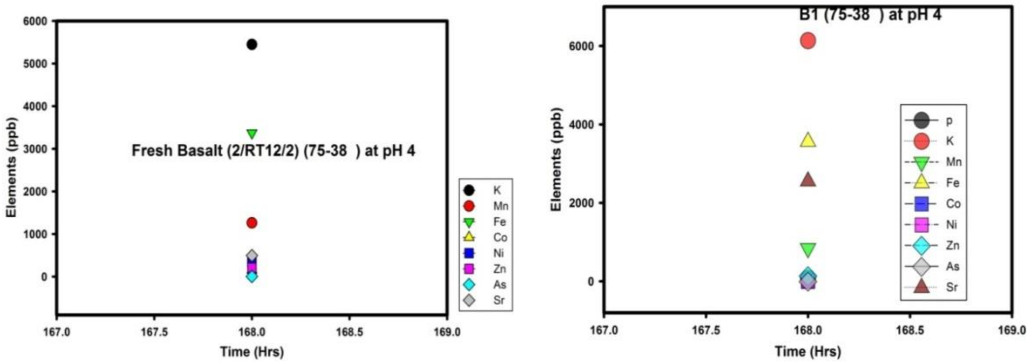


(g) (h)

Figure 15. Plot shows elemental concentration (a) A2 (125-75µm) pH4, (b) A2 (75-38 µm) pH4, (c) Fresh Basalt(2/RT12/2) (125-75 µm) pH4, (d) Fresh Basalt(2/RT12/2) (75-38 µm) pH4, (e) A2 (125-75 µm) pH6, (f) A2 (75-38µm) pH6 , (g) F.R A1 (125-75µm) pH6 and (h) F.R A1 (75-38µm) pH6

4.4.3 Comparison of elemental concentration among fresh and weather basalt



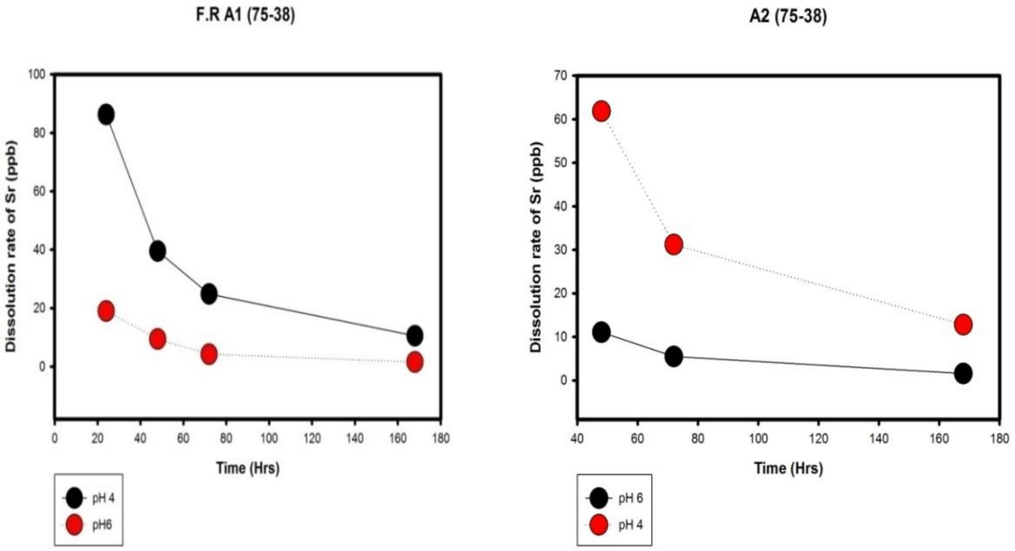
(a) (b)

Figure 16. Plot shows the comparison between fresh basalt (Fresh basalt (2/RT12/2) and weather basalt (B1) with same grain size, pH and time

4.4.4. Dissolution rate of Sr:

Table 9. Dissolution rate of Sr at pH 4 and 6 with 24, 48, 72 and 168 hours

Sample Name	Elements	pH	Rate of dissolution(ppb/hr)			
			24 hrs	48 hrs	72 hrs	168 hrs
Fresh basalt(2/RT1 2/2) (75-38 µm)	Sr	4	-	-	-	2.943024
F.R A1 (75-38 µm)	Sr	6	18.98505	9.425675	4.221853	1.579916
F.R A1 (75-38 µm)	Sr	4	86.2501	39.51774	24.83106	10.53385
A2 (75-38 µm)	Sr	6	-	11.06534	5.490232	1.582823
A2 (75-38 µm)	Sr	4	-	61.84022	31.21204	12.79948
B1 (75-38 µm)	Sr	4	-	-	-	15.24569



(a) **(b)**

Figure 17. Plot shows the dissolution rate of Sr in two different samples

Table 7 & 8 shows the ICP-MS data of different elements. In Figure 14 the plot (a) and (b) shows at low pH/ acidic condition the elemental concentration is observed to be high. e.g. In case of Sr, at 48hrs the concentration is ~500 ppb at pH 6 where as the concentration is ~ 6000 ppb. This shows that the rate of weathering is higher in the case of pH4, but the weathering rate is lower in case of pH 6. In case of Al, at pH4, the leached concentration reached to a level beyond the calibration level such that the data is not considered here. In case of plot (c) and (d) the concentration of leached element is higher in pH 4. At 168 Hrs, Sr has an higher concentration at pH 4. In the plot of (e), (f), (g), (h), (i) and (j) the dissolution rate of rock is higher at pH 4.

In Figure 15 the plot of (a) and (b) the Sr shows the higher concentration of ~9000 ppb for small grain size, where as higher grain size has only ~3500 ppb at 72 hrs.This particular sample shows that the higher dissolution rate for the smaller grain size is higher. The plot (c), (d), (e), (f), (g) and (h) shows very little variation in the elemental concentration with variation in the grain size in both pH 4 and pH 6. However the previous studies suggest an higher dissolution rate with smaller grain size. This was not observed probably due to the small time period of the experiment.

In Figure 16 the plot between (a) and (b) shows that in fresh basalt, Concentration of Sr is ~500 ppb, whereas in weathered basalt the Sr concentration is ~3000 ppb. Less compactness of weathered basalt or its already weak surface makes mineral dissolution easy as compared to the highly compact fresh basalt.

The Table 9 shows the dissolution rate of Sr at pH4 and pH6 at time 24 hours, 48 hours, 72 hours and 168 hours. In Figure 17 the dissolution rate is highest in the beginning that is the rate of dissolution is observed to be higher in the initial 24hrs then the dissolution rate is lower in the final time. The rate of F.R A1 (75-38 μm) at 24 hours is 18.98505 ppb/hr, but in 168 hours it will decrease to 1.579916 ppb/hr. The rate of A2 (75-38 μm) at 48 hours is 61.8402 ppb/hr, but in 168hours it will decrease as in case of F.R A1 (75-38 μm). Gradual decrease in dissolution rate of Sr is observed from most of the samples.

Chapter- 5
Conclusion

5.1 Conclusion:

The weather basalt (B1) is having lesser density compared to the other three fresher samples (F.R A1, A2 and Fresh Basalt (2/RT12/2)). The pH 4 changed to pH 4.5 and pH 6 changed to pH 7 during the 24, 48, 72 and 168 hours interval, except blank samples. From the XRD analysis we concluded the major minerals like Labradorite, Bytownite, Enstatite, Augite and other than this Olivine, Magnetite, Quartz is found as minor quantity, but Kaolinite is found as high percentage in weather basalt. In weather basalt (B1) the Plagioclase percentage is less, but in Fresher samples (F.R A1, A2 and Fresh Basalt (2/RT12/2) plagioclase present as a greater percentage. From ICP-MS analysis in acidic or low pH condition the leached elemental concentration is observed to be high. Grain size shows little variation in the elemental concentration due to the limited time period of experiment. The dissolution of Sr shows the dissolution rate is higher in the starting, but after that it decreased. Less compactness of weathered basalt or its already weak surface makes mineral dissolution easy as compared to the highly compact fresh basalt.

Future Work:

In this project work we got less time for the experiment, if the time is increased the result will be better. So in the future the dissolution analysis is continued with the same samples by extending the time by controlling the pH, temperature and grain size.

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