

Reconstruction of marine conditions in Precambrian-Cambrian (Pc-C) boundary using Shale Chemistry

Geochemical Study of Black shales from the Pc-C boundary

**MS Thesis Submitted to
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Certificate

This is to certify that this dissertation entitled **Reconstruction of marine conditions in Precambrian-Cambrian (Pc-C) boundary using Shale Chemistry** towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by **Ayush Nagar** at Indian Institute of Science Education and Research (IISER) Pune” under the supervision of **Dr. Gyana Ranjan Tripathy**, Assistant Professor, Earth and Climate Science Department” during the academic year 2016.

Declaration

I hereby declare that the matter embodied in the report entitled **Reconstruction of marine conditions in Precambrian-Cambrian (Pc-C) boundary using Shale Chemistry** are the results of the investigations carried out by me at the Department of Earth and Climate Science, Indian Institute of Science Education and Research (IISER) Pune, under the supervision of Name of the faculty and the same has not been submitted elsewhere for any other degree.

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Abstract

In this project, I have tried to find out the oceanic conditions during Precambrian-Cambrian(Pc-C) boundary by calculating the Redfield ratio using Black shale samples collected from Maldeota village of Dehradun and comparing it with the current average value of C:N:P ratio. After several experiments, the value of C: N: P was found to be very less in comparison to Redfield ratio, which might indicate a high quantity of oxygen present at the time of deposition.

Introduction

Reconstruction of past oceanic conditions and assessing its possible influence on biosphere have always been one of the major concerns of geologists. In particular, the knowledge of marine redox state at a specific time period may help us in understanding response of oceans to the environmental and climatic changes during that period. One of the major factors used to infer past marine redox conditions is oceanic productivity. The oceanic productivity refers to the total biomass produced in an ocean during a specific time period. The organic matter present in marine sediments is produced mainly by phytoplankton by converting inorganic carbon using photosynthesis. Intensity of oceanic productivity depends critically on the availability of major (i.e. Carbon, nitrogen and phosphorus) and minor (e.g. Fe, Mo, Cu, etc.) nutrients. The oceanic productivity plays a major role in global carbon cycle, since it helps in determining the amount of carbon taken out of the atmospheric and continental carbon into the marine system. Out of the large quantities of net organic matter produced by phytoplankton, only a fraction is exported to the deeper beds for sedimentation. The sinking of organic matter occurs mainly through the segregation of large quantities of phytoplankton cells, as well zoo planktonic faeces and remains (Bhushan et al. 2001). Significant fraction of the organic matter gets oxidized in the water column depending on the abundance of oxygen in the water; lack of oxygen often enhances the degree of preservation of carbon in the sediments.

Phosphorus, another important major nutrients that regulated the intensity of productivity in an oceanic basin. The major source of phosphorus into the oceanic system is the detrital flow. A small amount of Phosphorus is also transported through dust particles into the oceans. It must be noted here that under natural conditions, the inorganic phosphorus is mostly present in V oxidation state as phosphates (PO_4^{3-}) and polyphosphates. In case of organic compounds, phosphate ester bonds are used as linkage between different constituent molecules to form long, complicated compounds. Phosphorus is taken by the phytoplankton in the form of hydrogen phosphate (HPO_4^{2-}) and incorporated into the biomass. The soluble part of organic matter is then treated by bacteria to again yield phosphates.

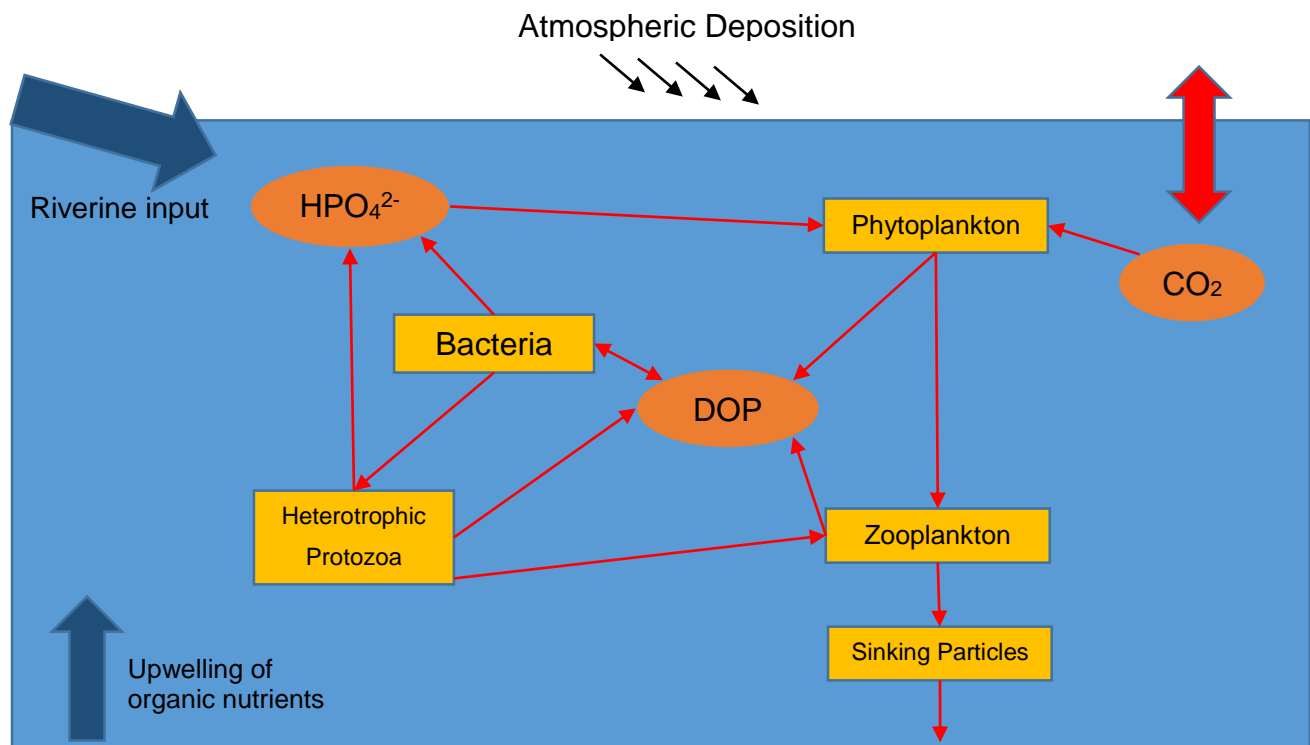


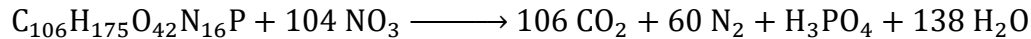
Figure 1: Phosphorus cycle in marine system (source: (Benitez-Nelson 2000))

The removal of Phosphorus from ocean surface occurs through fossils, adsorption of Phosphorus onto iron, sedimentary Phosphorus burial as well as authigenic Phosphorus minerals. The residence time of Phosphorus in the ocean is 20,000 to 40,000 years (Jahnke 1992) (Sigman et al. 2012).

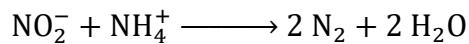
In marine ecosystems, the Nitrogen cycle is mainly driven by biochemical processes. The atmospheric Nitrogen is fixed by cyanobacteria and converted to organic material. This fixed Nitrogen is stored in Deep Ocean in the form of Nitrates (NO₃⁻). The upwelling of ocean brings some of these Nitrates back to the euphotic zone, where they act as a new source of Nitrogen along with atmospheric deposition, thus driving the export production. Some part of nitrogen is also transported to the ocean bottom via feces and remains of marine organism and converted into sediments (Gruber 2008a). The removal

of fixed Nitrogen takes place via de-nitrification and anammox, where nitrates are used for oxidizing and decomposing organic matter by bacteria in environments containing low levels of oxygen (Gruber & Galloway 2008). The residence time of Nitrogen in marine systems is less than 3000 years (Gruber 2008b). The reactions for de-nitrification and anammox are shown below:

Denitrification:

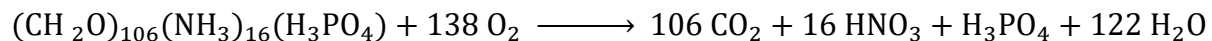


Anammox:



(Nitrogen in marine environment)

The C, N and P of marine organisms are mostly found to have a constant proportion in their abundances. Arthur Redfield proposed a relationship of macronutrients in algae as C: N: P ratio of 106:16:1. This ratio was later termed as Redfield Ratio. It describes the amount of macronutrients required for the optimum growth of phytoplankton. The nutrient uptake of phytoplankton can be described by the equation (Jorgensen et al. 2007):



From Redfield ratio, the optimum ratio of N: P should be 16:1. If the N: P ratio is significantly lower than 16:1, then it would indicate a limitation of available Nitrogen to the phytoplankton. Similarly, a significantly higher N: P ratio would indicate the lack of Phosphorus. These limitations might change the biological ecosystem, thus affecting phytoplankton biomass and species variation.

According to a paper authored by Sterner et al., which used >2,000 observations from lakes, coastal regions as well as off-shore marine regions from major places around the globe, the average values of C: P, N: P and C: N were 131, 18 and 6.6 in oceans (Sterner et al. 2008). The mean values of C: P, N: P and C: N data from various regions is shown below in the form of a table.

Oceans	C:P			N:P			C:N		
	Mean	N	SD	Mean	n	SD	Mean	n	SD
Atlantic	112	19	24	17	19	3	6.7	19	0.7
Bermuda	235	93	84		0			0	
Indian	101	159	37	15	159	5	6.5	159	1.2
Mediterranean	202	50	65	26	50	10	8.3	50	3.3
Hawaii	128	62	29	19	62	6	7.2	62	3.1
Sea of Japan	153	30	99	16	30	10	9.3	30	2.4
Combined	155	6	53	19	6	4	7.6	6	1.2

Table 1: Mean values of C: P, N: P and C: N from various regions around the globe (Sterner et al. 2008).

The C, N and P content of marine sediments can provide a useful clue for nutrient inventory of the ocean during their deposition period. Earlier studies have investigated these important constituents in organic-rich marine sedimentary rock and these datasets provide clues on paleo-ventilation pattern of the ocean (Murphy et al. 2000). Studies have also been conducted on the Precambrian-Cambrian boundary in the lesser Himalaya region and various Geochemical parameters, such as finding out the abundance of various elements during the Pc-C boundary (Banerjee et al. 1997) and geochronology of samples (Singh et al. 1999).

Objectives of the project

1. Geochemical (C, N, P) investigation of Himalayan black shales deposited at the Pc-C boundary to infer past seawater conditions.
2. Reconstruction of past-productivity using the inferred macronutrient inventories at that geological important time period.

Pc-C Boundary

The Precambrian-Cambrian boundary (541 Ma) is an important geological time period that witnessed significant bio-diversity. The Precambrian-Cambrian boundary has been

of much interest to researchers because of an exponential increase in the fossils found towards end of the Precambrian. Immediate after the Pc-C boundary records of both trace and body fossils indicate a drastic increase in the metazoan activity. This resulted in diversity and the origin of phyla (Marshall 2006a). It is possible that most of the modern phyla may have originated during this explosion (Valentine et al. 1999). But, despite its pivotal role in the evolutionary history, the origins and causes of Cambrian explosion remain controversial. The major issues which have been addressed are (1) The drastic increase in animal disparity and diversity, (2) Why was the explosion triggered around 543-542 Ma and why was the duration of this event tens millions of years (3) Why does this event appears unique(Marshall 2006b). There have been many speculations regarding the possible causes of Cambrian explosion, which we shall not discuss here.

Methodology

Black Shales are fine-grained, organic-rich and laminated sedimentary rocks. In general, Black shale contain ~1-10% organic content(Tourtelot 1979). They are deposited in deep ocean basins in anoxic conditions(less than 0.5mg/L according to USGS).

Sample Collection

Fresh Black Shale samples were collected from Maldeota village in Dehradun. The Black shale were taken from an abandoned PPCL open cast mine. Samples HM15-10 to HM15-21 were collected from this location. The samples were blackish and pyrite-rich in nature. The stratigraphic position of samples was in the Tal Formation, close to Krol-Tal boundary (at a distance of ~3m). The following figure 2 depicts the stratigraphic location of Pc-C boundary as well as the positing of Maldeota in India.

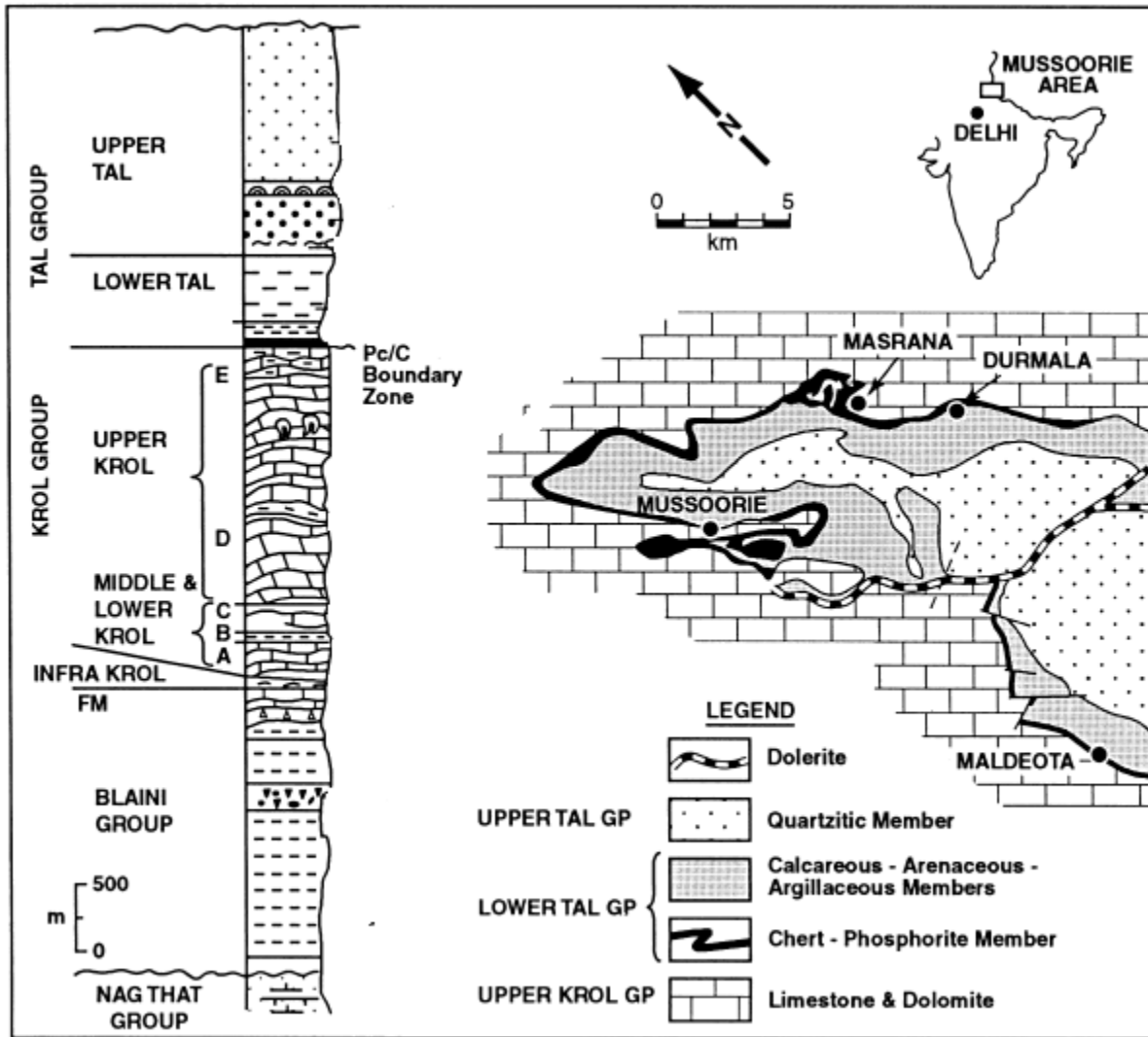


Figure 2: Position of Maldeota in Mussoorie Area as well as the stratigraphic positing of Pc-C boundary(Banerjee et al. 1997).

Methods

The various methods used in the project are described via flow chart in figure 3 below.

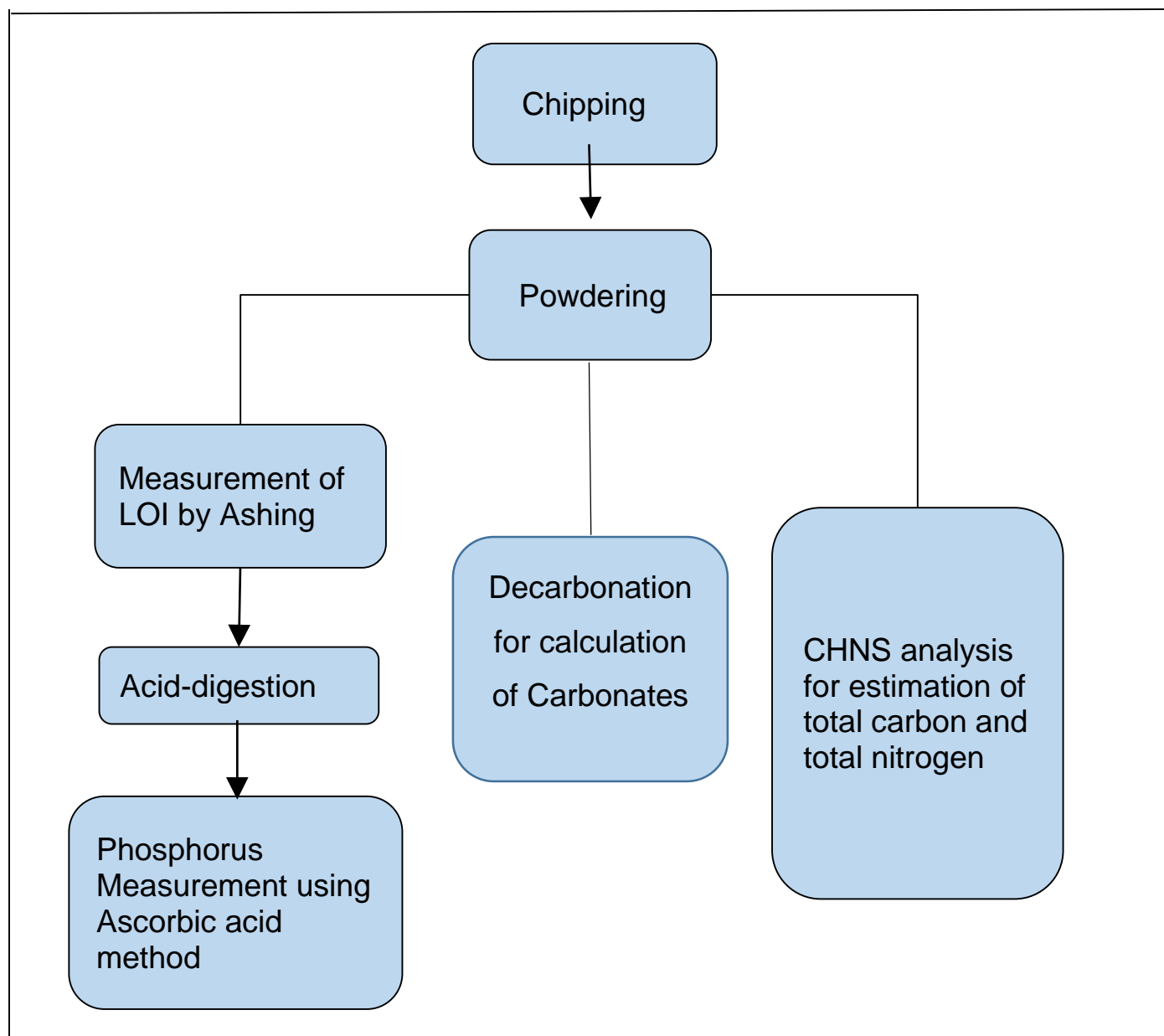


Figure 3: A flowchart depicting various stages of experimental procedure

Chipping

The collected samples were chipped using a hammer to remove their weathered portions, which might have caused a hindrance in their geochemical analysis. The non-weathered portions of the samples were then divided into two portions, and labeled A and B, to ensure the precision in various measurements. Thus, a total of 22 samples labelled from HM15-10A to HM15-21B were used for analysis.

Powdering

The chipped samples were then grinded using agate mortar pestle manually. For each sample, specific caution was taken to ensure minimum contamination from other samples using separate butter papers and filtering cloth(having pore size $\sim 100\mu\text{m}$), as well as proper cleaning after powdering of each sample.

Ashing for calculation of Loss by ignition (LOI)

Principle

The water content, organic carbon and carbonate content can be determined by using this process. The water vapor can be removed by heating near $80\text{-}100^\circ\text{C}$ or using silica gel. The organic carbon gets converted to carbon dioxide and ash after heating at $\sim 200\text{-}500^\circ\text{C}$. The removal of carbonate requires temperatures ranging from $\sim 700\text{-}900^\circ\text{C}$ (Rosenmeier 2001). Weight losses after heating at specific temperatures can thus be used to find out water content, organic carbon and carbonate content as required.

Procedure

At first, weight of labelled empty crucibles is recorded (there was no change in weight after labelling). Then $\sim 3\text{gm}$ of powdered samples were added to their respective crucibles and final weight was recorded. The samples were then kept in oven at 80°C for 4 hours. The crucibles were then kept in a desiccator containing heated silica gel overnight to remove any remaining water vapor. The weight of crucibles was recorded again and the difference was calculated. This process is used to determine and remove water from the samples. The crucibles were kept in a furnace for heating at 600°C for 4 hours. The samples weights are recorded again and subtracted from the weight obtained after removing from desiccator. This weight difference gives the organic carbon content in each sample.



Figure 4: Samples before heating in furnace (left) and samples after heating (right)

Acid-digestion method

Principle

The functions of various acids in dissolution of sample is explained below:

Hydrofluoric acid, HF: The function of HF is to dissolve silica to form SiF_6^{2-} . This reaction can be dynamic, hence HNO_3 is added to the Black shale powder before adding HF. Also, HF can react with Calcium present in Black shales to form an insoluble Calcium Fluoride, CaF_2 . The adding of HNO_3 before HF can therefore also prevent the formation of CaF_2 , since the Calcium ions will have reacted with nitrate ions instead.

Nitric acid, HNO_3 : Concentrated Nitric acid acts as an oxidizing agent for the dissolution of organic matter present in the samples.

Aqua Regia: Aqua regia is a solution of nitric acid and hydrochloric acid in the ratio 1:3. Aqua regia can dissolve gold and some of platinum group metals (Potts 1987).

Procedure

The samples were processed for acid-digestion in batches of 10, including 8 samples, containing one blank (empty container in which all cycles of acid were carried in a similar manner) and one repeat sample to measure errors in each batch. Around 300mg of each sample was measured in a labeled tarson container.

2 ml of HNO_3 is added to the containers and kept on a hot plate at 80°C and then 4 ml of HF is added to the mixture. The containers were then closed with tarson lids and kept at 80°C for 4 hours. After 4 hours, the lids are removed carefully and the solutions containing samples were heated at $\sim 110^\circ\text{C}$ till the samples appear jelly-like. After this, 6 ml of freshly prepared aqua regia is added to the containers and kept at 80°C for 4 hours after closing the lids. Again the solution mixture is dried until it becomes jelly-like. The whole process is repeated for 5-6 cycles till the samples completely dissolve. After this, at the end of aqua regia cycle, 4-5 ml of HNO_3 is added and kept for drying (the samples should fully dissolve in HNO_3). Then, 1 ml of HNO_3 is added to the dry residue and mixed with Millipore water. The solution is warmed for some time to dissolve the residue and then filtered in a 50 ml volumetric flask, which is then filled up to the mark. After shaking, the solutions are then stored in separate marked bottles.



Figure 5: Samples kept for acid-digestion.

Phosphorus measurement using Ascorbic acid method

Principle

Ammonium molybdate and Potassium antimonyl tartrate react with orthophosphate in acidic medium to form a heteropoly acid-phosphomolybdic acid, which reacts with ascorbic acid to form molybdenum blue complex, which can then be detected via UV-spectroscopy. The UV-absorption peak of phosphate (PO_4^{3-}) occurs at a wavelength of 880nm. The minimum detectable range of Phosphorus using this method is $10\mu\text{g/L}$ (Doolittle 2014).

Reagents

Sulphuric acid, H_2SO_4 , 5N: Add 12.72 ml of H_2SO_4 in 10 ml of Millipore water in a 100 ml volumetric flask (This is to dilute the acid before adding more water, since otherwise adding water to concentrated acid may lead to a violent reaction). Now, add Millipore water into the flask till it reaches the 100 ml mark.

Potassium antimonyl tartrate (PAT): Chemical formula: $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$. It may be noted here that the chemical used in the experiment was actually $\text{K}_2(\text{SbO})_2\text{C}_8\text{H}_4\text{O}_{10}\cdot 3\text{H}_2\text{O}$ instead of the prescribed chemical because of non-availability of PAT. 137 mg PAT was poured in 50 ml volumetric flask and Millipore water added to make-up.

Ammonium molybdate: 4 gm of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was taken in a 100 ml volumetric flask and Millipore water was added to make-up the volume. The solution is then shaken vigorously and kept overnight on an automatic shaker. This is to ensure that Ammonium molybdate gets dissolved properly (as its solubility product constant is low).

Ascorbic acid: 880 mg of Ascorbic acid was poured in a volumetric flask of 50 ml and Millipore water was added to fill it up to the 50 ml mark. This solution is stable for 1 week, if stored at 4°C .

Combined reagent: For the preparation of 100 ml combined reagent, the above reagents were added in the following amounts: 50 ml 5N H_2SO_4 , then adding 5 ml of Potassium antimonyl tartrate, then 15 ml ammonium molybdate was added to the solution. 30 ml ascorbic acid was then added to the solution mixture. Let it be noted that

the order of adding reagents should remain fixed as described above. This reagent is stable for 4 hours.

Stock Solution: Add 109.75 mg KH_2PO_4 into 250 ml volumetric flask and add Millipore water till it reaches the mark. This leads to the formation of 100 mg/L stock solution of Phosphorus.

Working solution of KH_2PO_4 : Working solution is prepared by first diluting stock solution to 50 mg/L and then taking 5 ml of 50 mg/L solution into a 100 ml volumetric flask and filling it up to the mark with Millipore water.

Procedure

The working solution was used to prepare 5 standards to test the samples. An Unknown solution of 0.24 mg/L Phosphorus was prepared separately from the Stock solution to cross-check the standards. 10 ml of standards and samples were taken in separate centrifuge tubes and 1.6 ml of combined reagent was added to them. After keeping the solution mixtures for $\frac{1}{2}$ hour, their Phosphorus concentration was measured using UV-visible spectroscopy(Doolittle 2014).



Figure 6: Preparation of reagents for phosphorus measurement.

Ultraviolet and Visible spectrophotometry

Principle

When an electromagnetic wave of radiation interacts with matter, many phenomena can occur, including reflection, refraction, absorption, transmission, fluorescence, phosphorescence as well as photochemical reactions. In general, it is preferable for only absorption to take place while using UV-visible spectroscopy.

The energy of a molecule or atom exists in discrete levels instead of a continuum. Thus, only photons of specific energy can be absorbed by the molecules/atoms. The total energy of molecules can be represented by:

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

Also, it must be noted that

$$E_{\text{electronic}} > E_{\text{vibrational}} > E_{\text{rotational}}$$

From figure 6, it is clear that the energy of the incident photons will determine the range of transition. For some molecules and atoms, the energy provided by UV-visible radiation is sufficient to bring about transitions between electronic levels. Since the energy of molecules and atoms is discrete, hence the energy of photon absorbed by the molecule or atom is equal to the energy required for an electron to jump from a lower electronic level to a higher electronic level. As the absorption of photon in UV and visible range often leads to a transition between electronic levels of a molecule or atom, hence the UV-visible spectroscopy is also called as electronic spectroscopy. Typical wavelength observed through UV-visible spectroscopy lies from 200-800 nm, though the UV-visible spectrometer used in the project had a maximum range of 1000 nm wavelength.

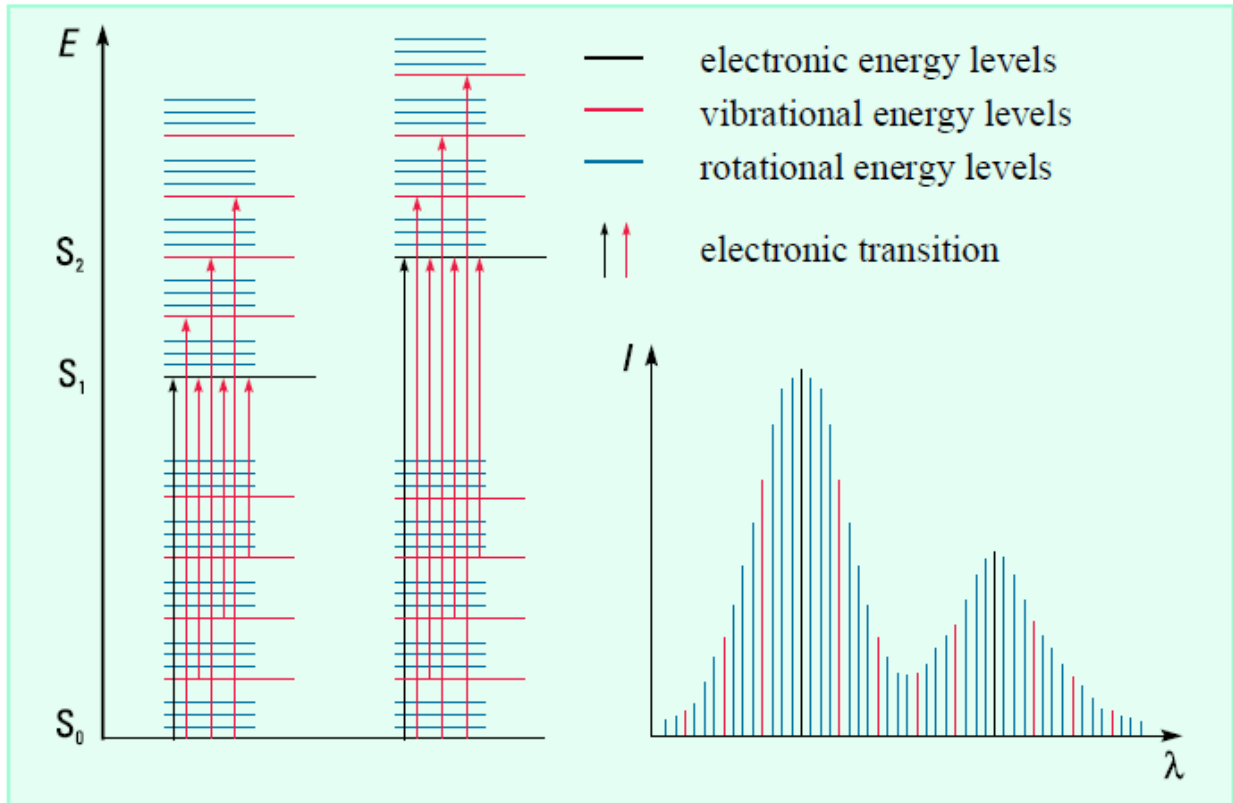


Figure 7: Various possible levels of electronic transitions in a molecule (Owen 1996).

The relation of absorbance and transmittance with intensity can be given by Lambert-Beer's law:

In a dilute solution, the absorbance of a molecule is proportional to its concentration at a given wavelength.

$$A = -\log T = \epsilon l c$$

Where A is absorbance, T is transmittance, ϵ is the absorptivity coefficient, l is the path length and c is the concentration (Kumar 2006) (Owen 1996).

Decarbonation

Principle

Inorganic carbon in the sample can be removed by dilute hydrochloric acid, HCl and the weight can be used as a way of calculating the amount of carbonate present in the

sample. Ultra sonication and Centrifugation are used to facilitate the reaction of HCl with inorganic carbon.

Procedure

1 gm of black shale samples were taken in separate centrifuge tubes and 11ml of 1N HCl was added to each sample. The samples were then kept for sonication for 1 hour. After this, the samples were kept for centrifugation for 15 minutes at 2000 rpm. This cycle was performed twice to ensure the full reaction of HCl with all of the carbonates present. The samples were then treated with Millipore water and the whole process was repeated three times. After this, the samples were dried in the oven at 80°C for 2 days and their final weights were taken to calculate the difference in weights.

CHNS analysis

CHNS elemental analyzer can be used to determine the total amount of carbon, hydrogen, nitrogen and sulphur present in organic materials. The analyzer contains two separate tubes, known as combustion and reduction tubes. In combustion tube, oxygen gas is passed at high temperature (~1000°C). Due to high temperature, oxygen oxidizes carbon, hydrogen, nitrogen and sulphur to carbon dioxide, water vapor, nitrogen gas (or its oxides) and sulphur dioxide respectively. Other elements like chlorine are also converted to hydrogen chloride gas. The elements not required can be absorbed by using various adsorbents in the combustion chamber. After the combustion, the products are then swept away from the combustion chamber by an inert gas like Helium, and passed through the reduction chamber. In reduction chamber, high purity copper at ~600°C is used to remove left over oxygen and to change the oxides of nitrogen into nitrogen gas. Afterwards, the products are passed through absorbents to remove other gases, leaving behind only carbon dioxide, nitrogen, water vapor and sulphur dioxide.

Results and Discussion

Results

It must first be noted here that the data presented here are very preliminary and more thorough and reliable analyses are underway to find precise and accurate datasets for these black shale samples from the Himalaya.

The total carbon percentage, measured using CHNS analyzer, had values ranging from 2.385 to 3.3, with an average value of 2.56. The carbonate percentage calculated using Decarbonation method amounted to most of the total carbon present, and it varied from 1.995 to 2.234, with average value 2.175. Total organic carbon (TOC), calculated by subtracting Carbonate from total carbon content only amounted to a small portion with values ranging from 0.104 to 0.644 with considerable variance over the samples.

Average total organic carbon was found to be 0.354. An alarmingly high value of percentage Loss by ignition (LOI), with an average value of 5.46 indicates an error either in the measurement of Carbonate percentage or the calculation of total carbon percentage, if the measurement of loss by ignition is accurate. Total Nitrogen percentage was calculated using CHNS analyzer. The Nitrogen values varied from 0.081 to 0.334, with an average value of 0.14. Similarly, total Phosphorus percentage was found using ascorbic acid method and a UV-visible Spectrophotometer. Phosphorus values ranged from 0.032 to 0.7135 with an average of 0.2855.

From these data, the average values of $C_{org}:N$, $N:P$ and $C_{org}:P$ for the samples were found to be 2.81, 1.49 and 1.44 respectively.

The table showing various data collected from the experiments is given below:

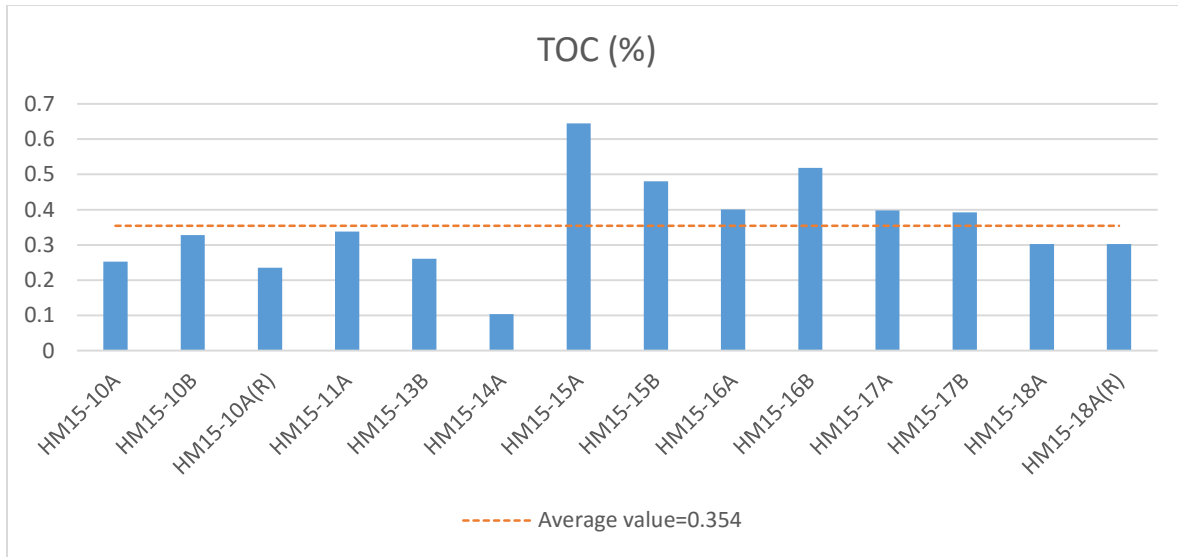
Sample No.	Total C%	Carbonate (%)	TOC (%)	LOI (%)	Total N%	Total P (%)
HM15-10A	2.486355	2.234069561	0.2522859	4.598	0.1208774	0.623003
HM15-10B	2.46945	2.141783567	0.3276662	4.7347	0.0987551	0.617678
HM15-10A(R)	2.46945	2.234069561	0.2353802	4.7347		0.644302
HM15-11A	2.527427	2.189873418	0.3375533	4.4929	0.1082962	0.649627

HM15-11B	2.540124			4.117	0.1072168	0.665602
HM15-13B	2.403892	2.14348758	0.2604047	4.57105	0.1117369	0.207668
HM15-14A	2.434795	2.330616403	0.1041786	4.4059	0.1510083	0.713525
HM15-15A	2.639789	1.995395242	0.6443934	6.338259	0.1242663	0.202343
HM15-15B	2.646034	2.165881004	0.4801529	6.386445	0.1428993	0.207668
HM15-16A	2.579498	2.179176755	0.4003216	6.304203	0.1287594	0.197018
HM15-16B	2.550099	2.031170158	0.5189288	6.164612	0.1252816	0.212993
HM15-17A	2.641256	2.243270189	0.3979856	6.170781	0.114003	0.223642
HM15-17B	2.617918	2.225875806	0.3920421	6.18062	0.1905682	0.197018
HM15-18A	2.468291	2.165881004	0.3024102	5.001667	0.1660933	0.175719
HM15-18A(R)	2.468291	2.165881004	0.3024102	5.001667	0.1660933	0.202343
HM15-19A	3.301076			5.8842975	0.3341321	0.031949
HM15-19B	2.689521			6.3877355	0.1287779	0.042599
HM15-20A	2.441585			6.3636364	0.1736565	0.042599
HM15-20B				6.361829		0.042599
HM15-21A	2.476218			4.312842	0.0904706	0.047923
HM15-21B	2.385462			6.2107697	0.0809975	0.047923
Average	2.561827	2.17474509	0.3540081	5.4630292	0.1402047	0.28551148

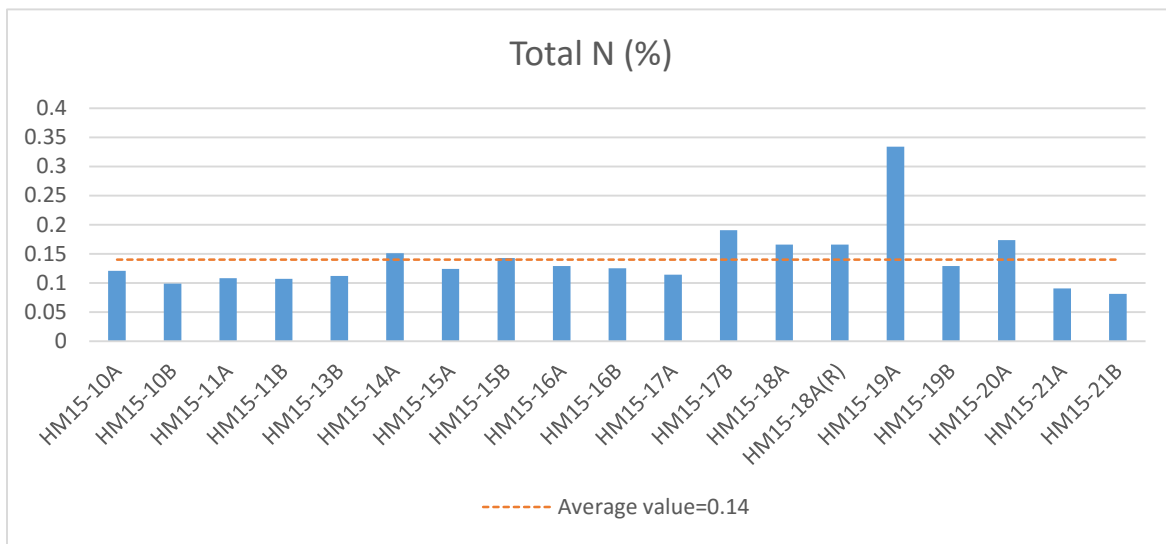
Table 2: Percentage values of Total Carbon, Carbonate, Total organic carbon (TOC), Loss of ignition (LOI), Total Nitrogen and Total Phosphorus

The plots for values of C_{org} , N and P as well as $C_{org}:N$, $N:P$ and $C_{org}:P$ are given below in figure 7(a-i).

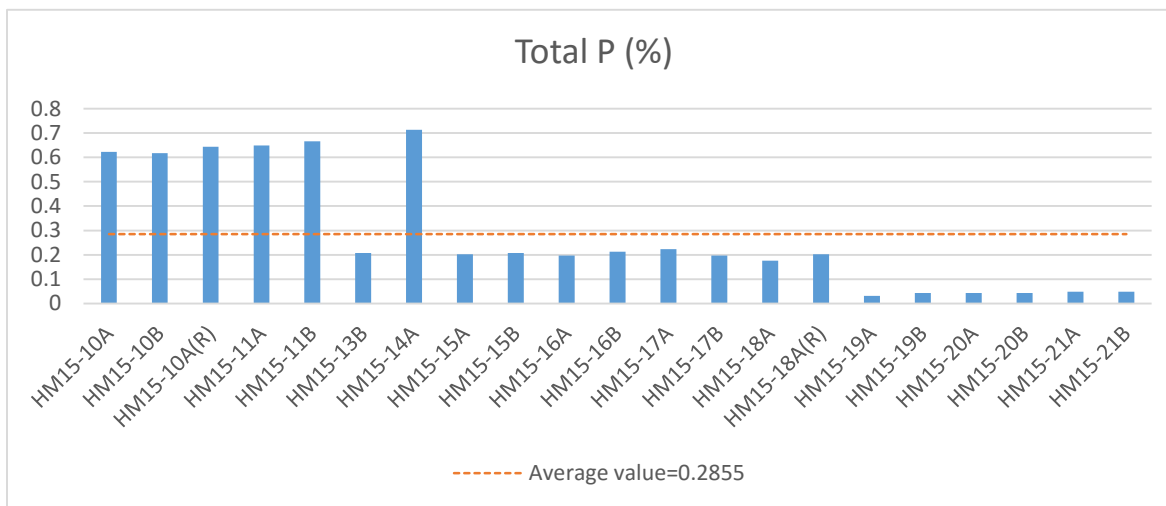
(a)

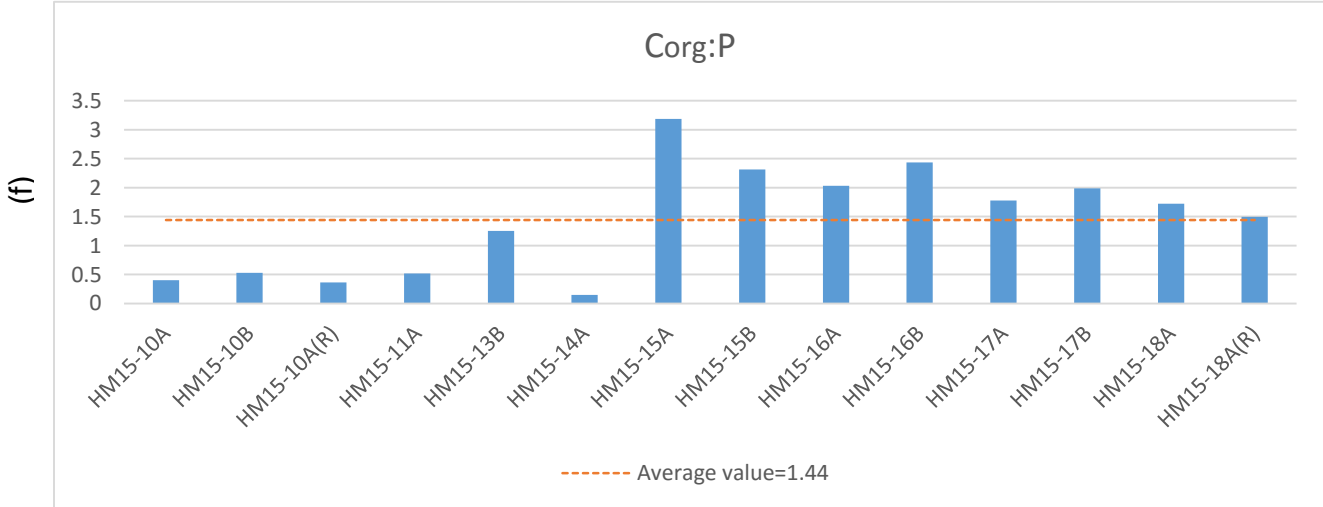
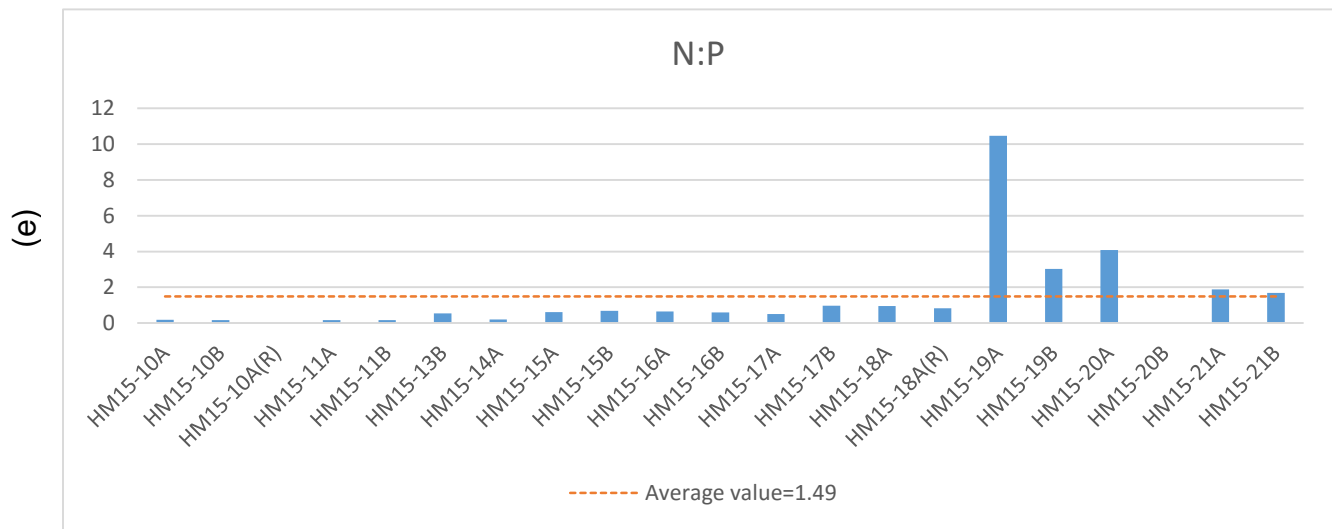
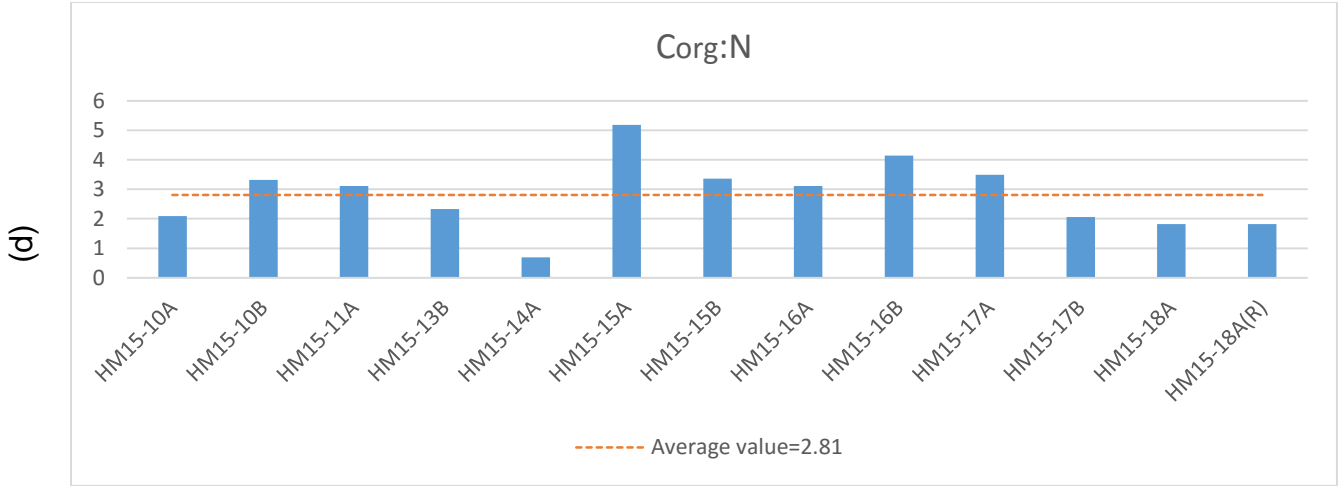


(b)



(c)





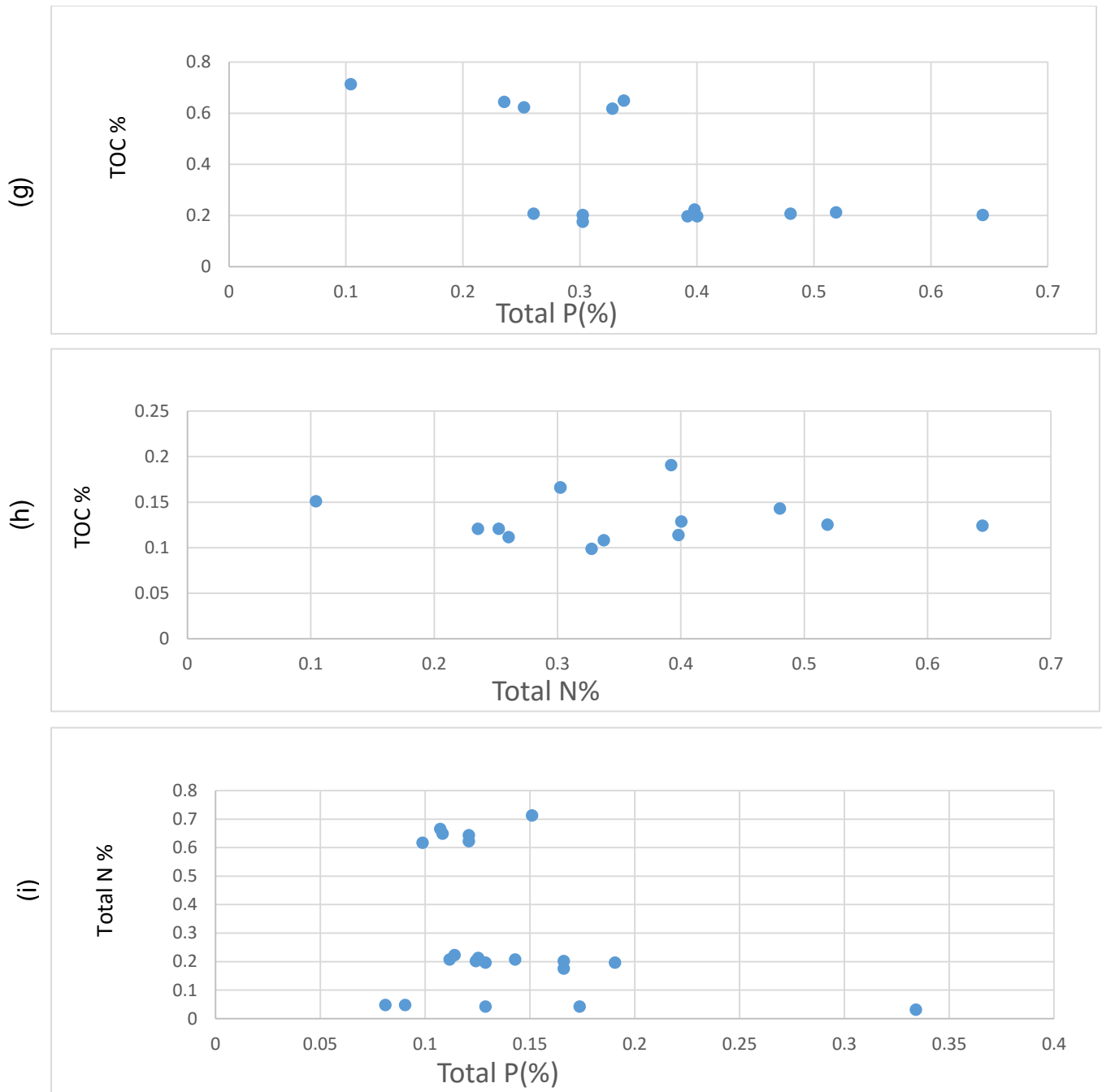


Figure 8: (a-c) Plots of C_{org} , N, P versus the sample numbers, (d-f) Plots of $C_{org}:N$, $N:P$ and $C_{org}:P$ versus sample numbers, (g-h) Plot of TOC versus Total P and Total N, (i) Plot of Total N versus Total P.

Discussion

The Redfield $C_{org}:N:P$ atomic ratio is 106:16:1. Thus, the values of $C_{org}:N$, $N:P$ and $C_{org}:P$ are 6.625, 16 and 106. There is an enormous contrast when compared to $C_{org}:N$, $N:P$ and $C_{org}:P$ values of 2.81, 1.49 and 1.44 observed from our experiments. This gives us a C: N: P value of 2:1.035:1 for our samples.

The less value of $C_{org}:N$ ratio indicate lesser value of carbon in comparison to nitrogen, which might be due to lesser preservation at the time of deposition because of an abundance of oxygen content, which may have oxidized most of the organic carbon to carbon dioxide. Another possible reason could be high nitrogen precipitation at that point of time in comparison to carbon.

The very low values of ratios of $N:P$ and C_{org} indicate high phosphorus content in the black shale samples. A possible for this may be better preservation of phosphorus in comparison to nitrogen followed by carbon. This explanation can also explain higher values of nitrogen as compared to carbon, but doesn't rule out the possibility of high oxygen availability at the time of deposition.

Conclusion

The low value of 2:1.035:1 for C:N:P ratio indicate that organic carbon deposited in the black shale samples in Precambrian-Cambrian boundary is very low compared to nitrogen and phosphorus, which may possibly be due to presence of a large amount of oxygen at the time of deposition, which could have oxidized most of carbon present. Another possible reason would be a better preservation of phosphorus in comparison to nitrogen followed by carbon.

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