Report

X-Ray Diffraction (XRD)

Mineral identification of rock samples from Chhota Sighri glacial moraine in Western Himalayas using XRD

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Abstract:

X-ray diffraction (XRD) is a very useful technique to determine the structure of unknown materials, physical and chemical properties of materials. The monochromatic beam of X-rays scatters from the set of lattice planes to produce constructive interference. Peak positions can be used to determine the minerals. This report summarizes the development, functioning, sample preparation, experimental arrangements, applications and limitations of the technique, X-Ray Diffraction.

Introduction:

In 1895, WC Rontgen discovered X-rays, which was later realized by other scientists that X-rays can be the correct wavelength for diffraction. Today about 1,000,000 material data sets have been collected, that contains diffraction, crystallographic and bibliographic data, as well as experimental, instrument and sampling conditions, and select physical properties in a common standardized format at International Centre for Diffraction Data (ICDD) or formerly known as (JCPDS) Joint Committee, organization that maintains the database of inorganic and organic diffraction spectra's.

X-ray diffraction is now a common technique for the study of atomic spacing and crystal structures. It does not requires any contact, and it is virtually non-destructive. Photons of X-rays with a wavelength in the nm range are ideal for electromagnetic radiation to be diffracted, as the spacing between the atoms is of the same order as wavelength.

Solid matters can be amorphous or crystalline. In amorphous materials, Atoms are arranged in a random way like glass. In Crystalline materials, Atoms are arranged in a regular pattern, and the smallest volume element, called Unit cell, is repeated in three dimensions and describe the crystal. Due to the periodic arrangement of atoms the X-rays will be scattered only in certain directions when they hit the formed lattice planes (formed by atoms). High intensity peaks are found in the diffraction pattern.

XRD Theoretical Aspects

X-ray diffraction (XRD)

It is a non-destructive method used for the study of nanomaterials with inter-atomic spacing that is of the same order of the wavelength of X-rays. X-rays can be generated by bombarding a target such as Cu, Mo, Fe, etc. with an electron beam. The electrons can be produced by heating a metal filament which then emits electrons and then accelerated towards the target. X-rays spectrum will be generated that consists of intense peaks on a continuous background, which can be utilized as monochromatic radiations and to be used for X-ray diffraction studies.

X-ray beams are directed at a crystal which interacts with the electrons of the atoms in the crystal. The electrons oscillate and become secondary sources of EM radiations. The waves emitted by the electrons have the same frequency as the incoming X-rays so, there can be constructive or destructive interference.

Bragg's Law:

Laue diffraction equation states that when thin X-ray beams impinge on a crystal, then for certain wavelength, oriented to proper angle to a group of planes so regularly spaced spots are produced on a film, which are centered on a central image from the beam, which passes through undeviated. Bragg's is a special case of Laue Diffraction.

$$n\lambda = 2d \sin\theta$$

It is the relation between the wavelength (λ) of the reflected X-ray, the spacing between the atomic planes (d) and the angle of diffraction (θ).
The wavelength of radiations has to be the same order as the spacing of the grating, and scattering should be in a specular fashion by the atoms of a crystalline system and undergoes constructive interference.

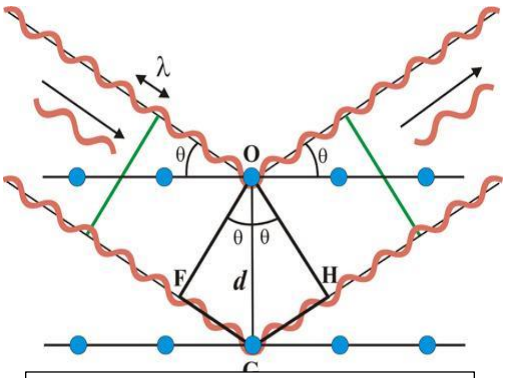


Figure: Bragg's law

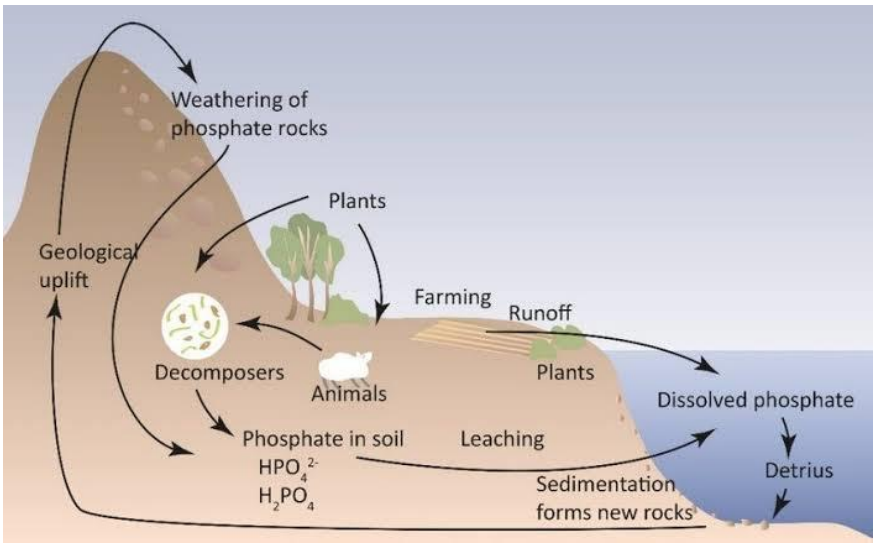
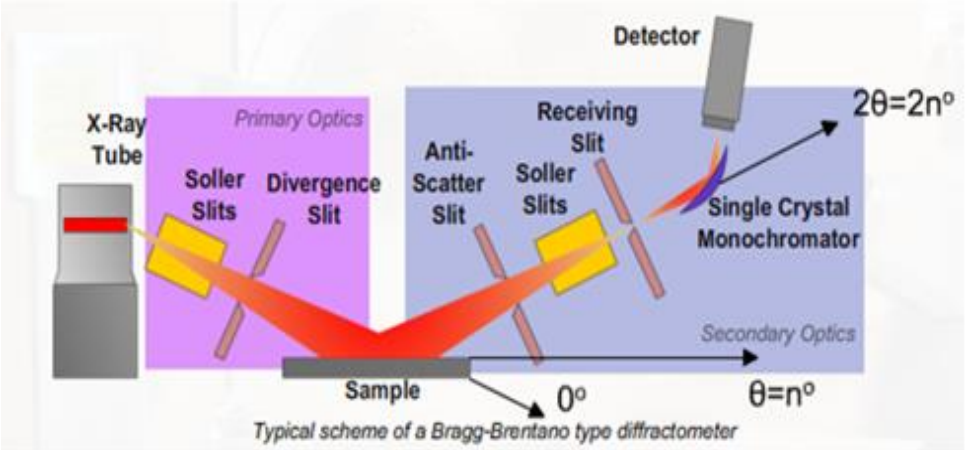


Figure: phosphorus cycle.
Reference: *Pan-Eurasian Experiment (PEEX)*

Phosphorous Cycle:

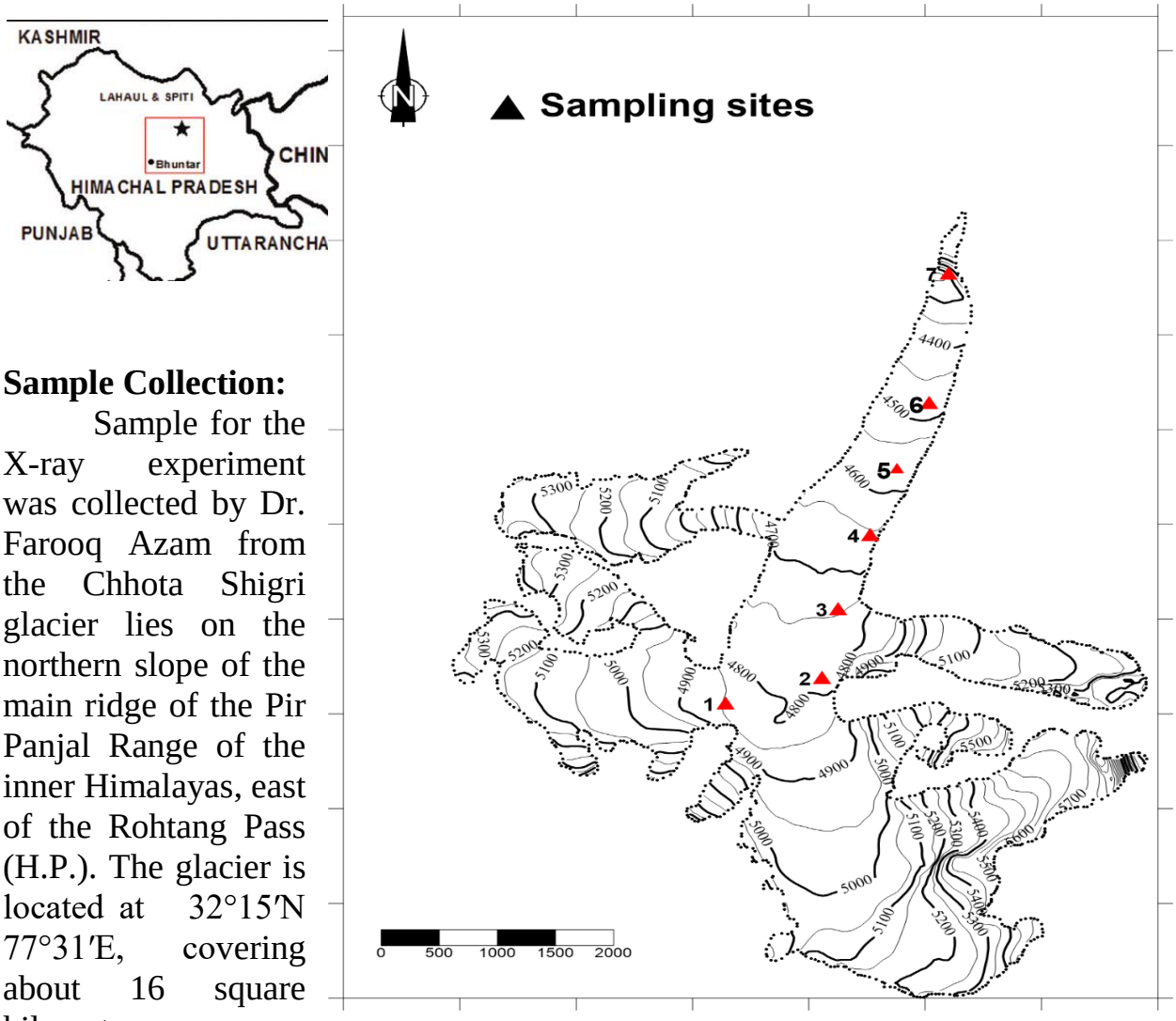
The movement of phosphorous throughout the lithosphere, hydrosphere, and biosphere is called phosphorous cycle. It is an extremely slow process, extraction of phosphorous by weathering of rocks, then due to weather events phosphorous washed into the soil. Living organisms absorb phosphorous from the soil and grow, then decomposition results in the return back to the environment. Phosphorous is essential for the growth of both plants and animals. Phosphorous is required in formation of nucleotides, which comprises of DNA and RNA molecules. Several human activities are affecting the phosphorous cycle such as the use of fertilizer and artificial eutrophication etc.

Experimental Arrangement:



Typical scheme of a Bragg-Brentano type diffractometer

Modern instruments use minicomputer for control, data acquisition, and data processing. In the figure X-ray source and the detector are on the same side of the sample. This geometric arrangement is known as the Bragg-Brentano Parafocusing system used in diffractometers. Soller silts reduce the axial divergence and divergence silt reduces the height divergence. Monochromators are used to absorb Kβ and white radiation. Only Kα1 and Kα2 radiations are allowed to pass through. The diffraction angle 2θ is the angle between the incident and diffracted X-rays. A typical diffraction spectrum is a plot of reflected intensities vs deflected angle 2θ.



Sample Collection:

Sample for the X-ray experiment was collected by Dr. Farooq Azam from the Chhota Shigri glacier lies on the northern slope of the main ridge of the Pir Panjal Range of the inner Himalayas, east of the Rohtang Pass (H.P.). The glacier is located at 32°15′N 77°31′E, covering about 16 square kilometers area. Approximately 35 square kilometers is the total drainage area of the glacier.

Figure: Chhota shigri glacier.
Red spots are the sample collecting sites.

Sample Preparation:

Sample preparation is the most important and crucial step in X-ray powder diffraction. In this, we remove the undesirable substances and use proper techniques to obtain desired particle size and orientation. Several books are available for different types of sample preparation.

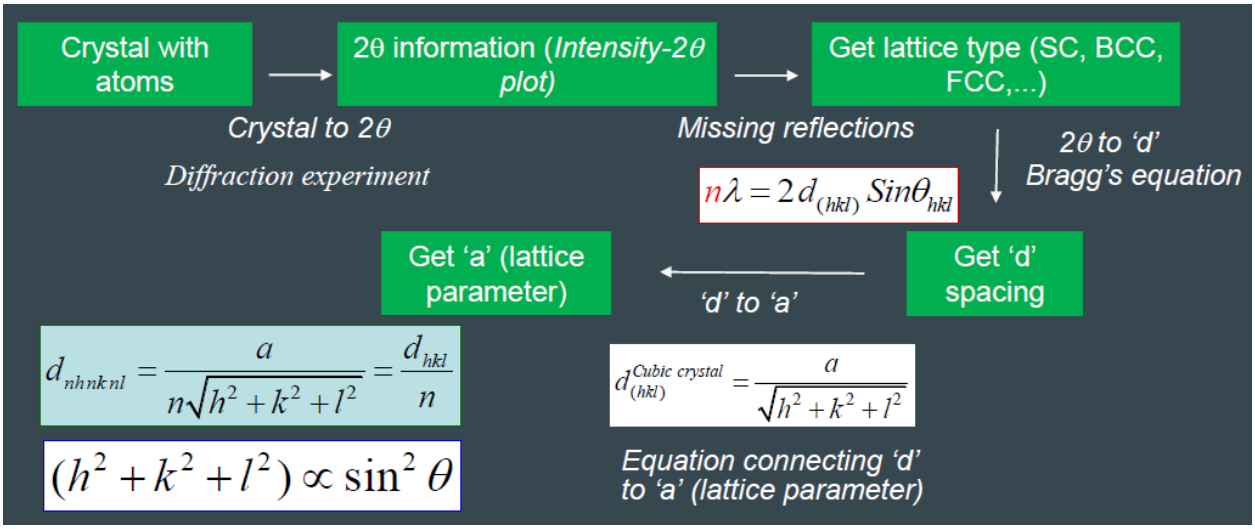
The rock/mineral sample crushed into small pieces and then ground into a fine powder and sieved (45 µm) to obtain homogeneous particle size. Agate mortar and pestle can be used to produce fine powder for soft minerals. If the mineral is hard mechanical grinding with Micronizing Mill may be required to get to desired particle size. The particle (favorable) size will be between 10µm to 50µm.

The crystallites have to be in different 'random' orientations in the powder sample. The coherent X-ray beam is diffracted by these crystallites at various angles to the incident direction. Angle of reflections and the intensities of reflections can be recorded by a diffractometer.

After performing XRD on powder samples we can identify the minerals, either doing calculations manually or using the software.

Manual Identification:

Following steps have to be followed in manual identification of minerals in powder samples:



Using these both relations:

$$d_{nhnknl} = \frac{a}{n\sqrt{h^2+k^2+l^2}} = \frac{d_{hkl}}{n} \qquad n\lambda = 2d_{(hkl)}Sin\theta_{hkl}$$

We can deduce that:

$$(h^2 + k^2 + l^2) \propto \sin^2\theta$$

The missing reflections:

There are different types of crystal structures such as Simple Cubic (SC), Face Centred (FCC) and Body Centred (BCC) etc. The structure changes as the presence of additional atoms in the unit cell. Due to that additional atom, there are missing reflections. The wave scattered from different planes is out of phase due to that additional atom.

Crystal is a transitional periodic arrangement of the motif at lattice points. The position of peaks tells us about the type of lattice and the intensity of peaks tells us about the motif.

The reflections which may be present and the missing reflections due to additional atoms in the unit cell are in the table below:

Bravais Lattice*	**Reflections which *may be* present**	**Reflections necessarily absent**
Simple	All	None
Body centred	$(h + k + l)$ even	$(h + k + l)$ odd
Face centred	h, k and l unmixed *(i.e. all even or all odd)*	h, k and l mixed
End centred *(C centred)*	h and k unmixed *(centering along 'l' index)*	h and k mixed

The Bragg's equation tells us about the position of diffraction peaks (θ), so using the relation deduced above we can find the ratio of $(h^2 + k^2 + l^2)$, using $\sin^2\theta$ values.

Possible ratios of $(h^2 + k^2 + l^2)$ derived from extinction rules:								
SC	**1**	**2**	**3**	**4**	**5**	**6**	**8**	**…**
BCC	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**…**
FCC	**3**	**4**	**8**	**11**	**12**	**…**		

Here is example from the book Elements of X-Ray Diffraction by B.D. Cullity & S.R. Stock.

#	**2θ**	**θ**	**Sinθ**	**Sin2 θ**	**ratio**	**Index**	**d**
1	38.52	19.26	0.33	0.11	3	111	2.34
2	44.76	22.38	0.38	0.14	4	200	2.03
3	65.14	32.57	0.54	0.29	8	220	1.43

4	78.26	39.13	0.63	0.40	11	311	1.22
5	82.47	41.235	0.66	0.43	12	222	1.17
6	99.11	49.555	0.76	0.58	16	400	1.01
7	112.03	56.015	0.83	0.69	19	331	0.93
8	116.60	58.3	0.85	0.72	20	420	0.91
9	137.47	68.735	0.93	0.87	24	422	0.83
10	163.78	81.89	0.99	0.98	27	333	0.78

Now from the XRD experiment we has 2θ values , using which we find sin2θ values and the ratio of sin2θ, from there we can find the lattice type after matching with ratios table of allowed reflections.

Using $\lambda = 2d\sin\theta$

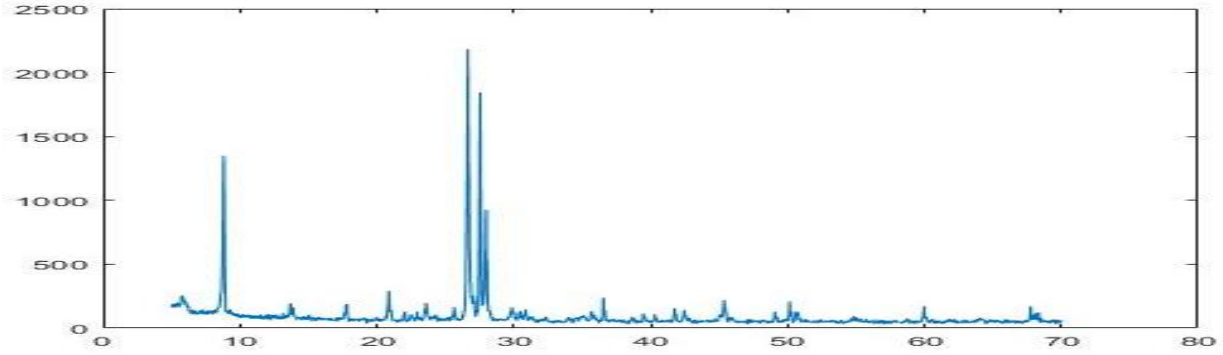
$1.54 = 2d_{111}\sin\theta_{111} = 2a/1.73 * 0.33$

$a = 4.04$ Å ⟶ Al (after matching with the database)

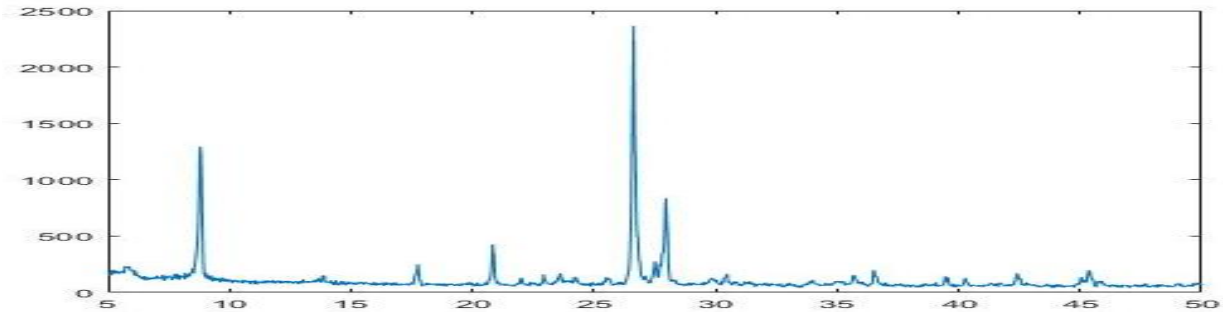
Diffraction Pattern:

After performing the XRD on sample rocks, the following diffraction pattern are observed:

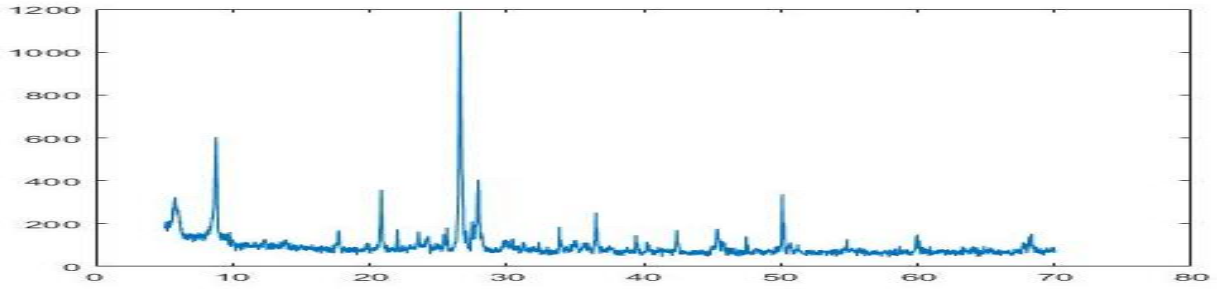
(Y-axis have intensities and X-axis have position (2θ) values on them)



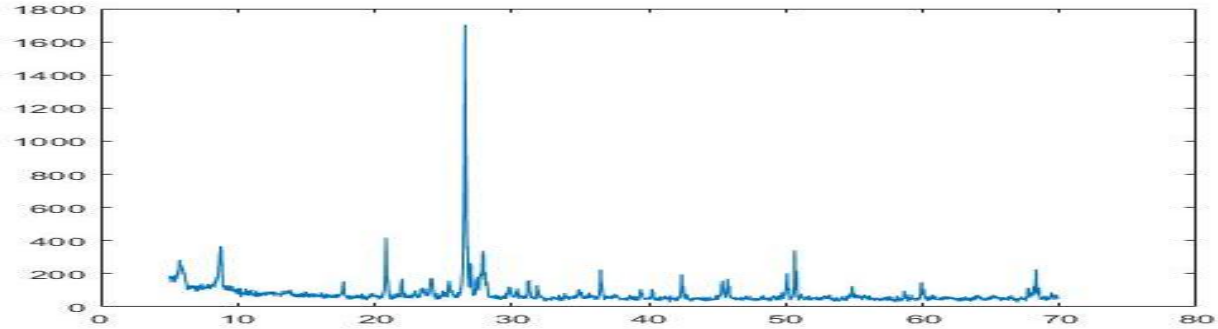
Sample No. 2: Diffraction Pattern



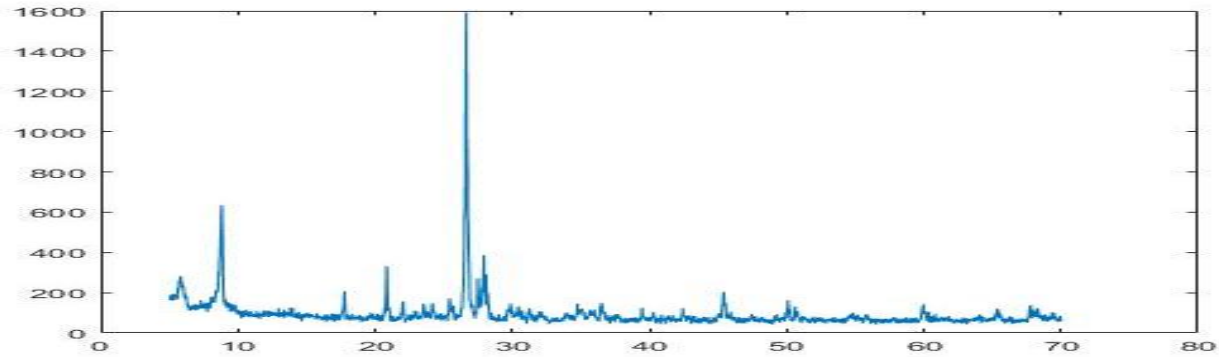
Sample No. 3: Diffraction Pattern



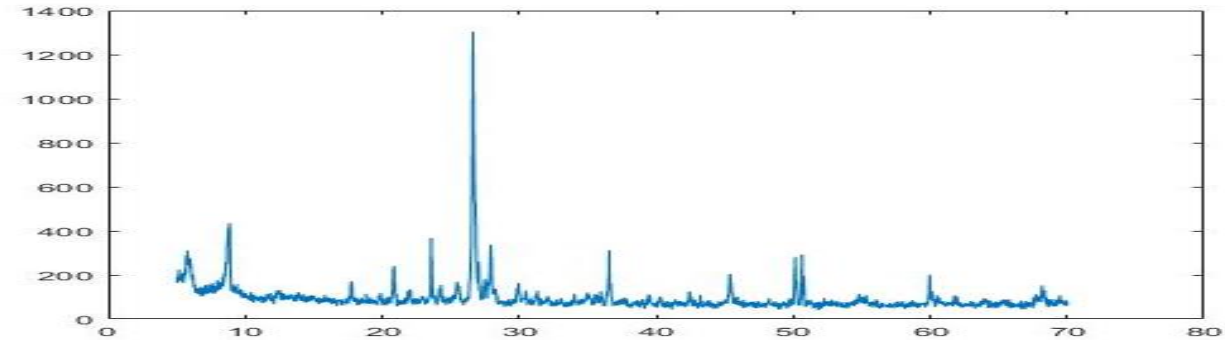
Sample No. 4: Diffraction Pattern



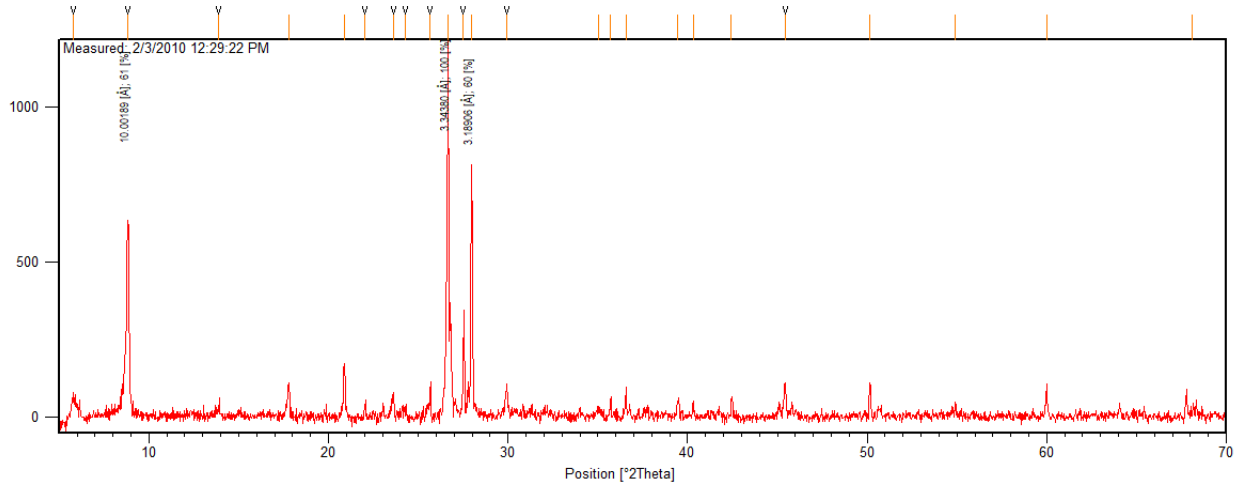
Sample No. 5: Diffraction Pattern



Sample No. 6: Diffraction Pattern



Sample No. 7: Diffraction Pattern

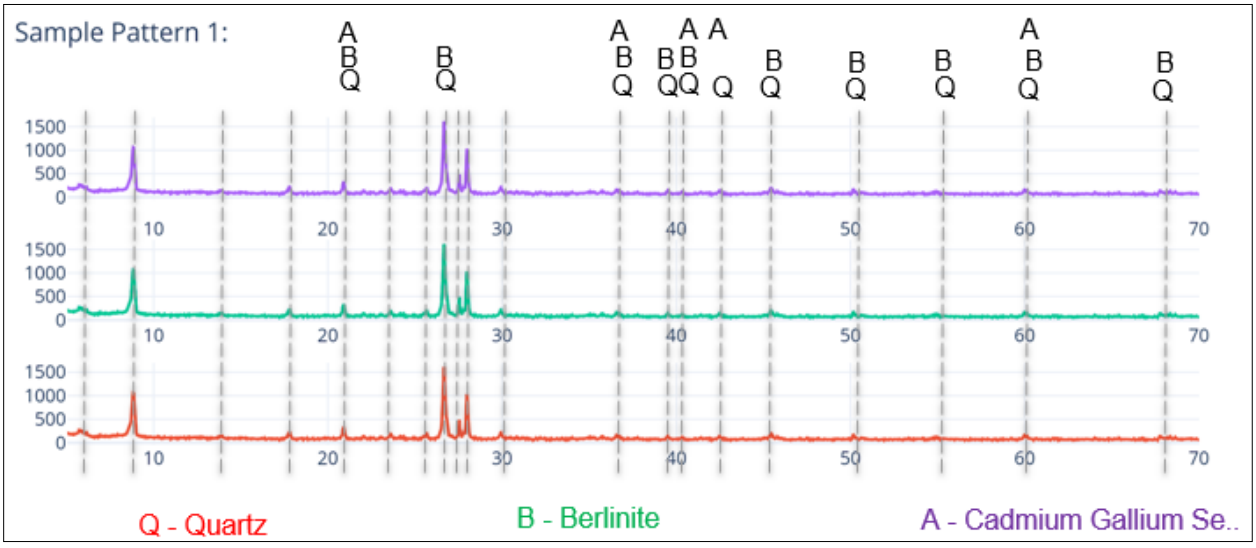


Sample No. 1: Diffraction Pattern

The peak values will be used to find the minerals present in the sample. Here, we used X-pert High score software to find out the minerals.

Steps performed in the identification of minerals on X-pert High score are as follows:

- Import .CAF file, which was obtained after XRD of the powder sample.
- Subtract the background from the diffraction pattern, due to presence of any liquid or amorphous solid.
- Strip K-alpha2 rays, for accuracy (Kα has a combination of Kα1 and Kα2 rays)
- Search for peaks by defining a threshold intensity
- Match the peaks with the data base to identify the minerals present.



In the figure above, we have three minerals quartz, Berlinite and Cadmium Gallium Selenium and the diffraction pattern. Some peaks matched with these three minerals as denoted in the figure.

On the basis of matched properties reference patterns are examined and scored. Some peaks matched with all the three minerals and some matched with none of them.

Results:

In the table below we have the minerals present in sample, results after matching the diffraction pattern with the database using software:

Sample No.	Compound Name	Chemical Formula	Score
1.	Quartz	$Si\ O_2$	73
	Berlinite, syn	$Al\ P\ O_4$	43
	Cadmium Gallium Se..	$Cd\ Ga_2\ Se_4$	41
2	Silicon Oxide	$Si\ O_2$	66
	Poly(4'-methoxybip..	$(\ C_{30}\ H_{31}\ Br\ O_6\ )_n$	44
	Graphite, syn	C	44
	Silicon Sulfide	$Si\ S_2$	42
3	Silicon Oxide	$Si\ O_2$	62
	Graphite, syn	C	42
4	Quartz	$Si\ O_2$	61
	Graphite, syn	C	39
	Silver Sulfide	$Ag_2\ S$	33
5	Silicon Oxide	$Si\ O_2$	58
	Zinc bis(hydroxyan	$C_{30}\ H_{14}\ N_4\ O_4\ Zn$!..	37
	Silicon Sulfide	$Si\ S_2$	36
	2-Thiohydantoin	$C_3\ H_4\ N_2\ O\ S$	34
	Fersilicite, syn	Fe Si	33
6	Quartz	$Si\ O_2$	65
	Cobalt Oxide	Co O	45
	Vanadium Hydride	$V\ H_2$	44
	Cobalt Nickel Oxide	Co O ! Ni O	41
	Cuprite	$Cu_2\ O$	40
7	Quartz	$Si\ O_2$	62
	Silicon Iodide	$Si\ I_4$	40
	2-Thiohydantoin	$C_3\ H_4\ N_2\ O\ S$	38
	Graphite, syn	C	37

As discussed above, rocks are the sources of phosphorous in the phosphorous cycle and we can see in the table about presence of phosphorous in the rocks. The minerals such as Berlinite which contain phosphorous present in the sample. When

there will be floods or glacial outburst the rock sediments mixes with the soil so as phosphorous.

Conclusion:

X- ray diffraction (XRD) is a non-destructive used to determine structural properties like lattice parameters, strain, grain size, phase composition, preferred orientation etc. on a wide variety of minerals. It is mainly used to determine the crystal structure of an unknown material. XRD provides a high accuracy for d-spacing calculations. There are proved, well organized and comprehensive database available for thousands of materials. XRD have some limitation such as homogeneous material is best for the identification of minerals etc. Overall XRD is very useful for mineralogical analysis, crystallographic characterization and can be done in situ.

References:

- Cullity, B. D., & Stock, S. R. (2001). *Elements of x-ray diffraction*. Upper Saddle River, NJ: Prentice Hall.
- https://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html
- Sharma, R., D. Bisen, U. Shukla, and B. Sharma. "X-Ray Diffraction: A Powerful Method of Characterizing Nanomaterials". *Recent Research in Science and Technology*, Vol. 4, no. 8, Oct. 2012.
- Bunaciu, Andrei A. & UdriŞTioiu, Elena & Aboul-Enein, Hassan. (2015). *X-Ray Diffraction: Instrumentation and Applications.* Critical reviews in analytical chemistry / CRC. 45. 10.1080/10408347.2014.949616.
- Stibal, Marek & Tranter, Martyn & Telling, Jon & Benning, Liane. (2008). *Speciation, phase association and potential bioavailability of phosphorus on a Svalbard glacier*. Biogeochemistry. 90. 1-13. 10.1007/s10533-008-9226-3.
- Lappalainen, Hanna & Kerminen, Veli-Matti & Petäjä, Tuukka & Kurten, Theo & Baklanov, Alexander & Shvidenko, Anatoly & Bäck, Jaana & Vihma, Timo & Alekseychik, Pavel & Andreae, Meinrat & Arnold, Stephen & Arshinov, Mikhail & Asmi, Eija & Belan, B. & Bobylev, Leonid & Chalov, Sergey & Cheng, Yafang & Chubarova, Natalia & de Leeuw, Gerrit & Kulmala, Markku. (2016). *Pan-Eurasian Experiment (PEEX): Towards a holistic understanding of the feedbacks and interactions in the land-Atmosphere-ocean-society continuum in the northern Eurasian region.* Atmospheric Chemistry and Physics. 16. 14421-14461. 10.5194/acp-16-14421-2016.