

## X-Ray Diffraction in Mineralogical Research

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### Abstract

A brief account of role of X-ray diffraction (XRD) in mineralogical research with special reference to radioactive and atomic minerals is given. Aspects of research methodology such as sample preparation, analysis time, limitations, search match methods for identification, and complimentary techniques are also given. The most common applications of XRD in mineralogical researches related to radioactive/atomic minerals include identification of primary and secondary uranium and associated ore and gangue minerals, determination of the oxidation grade of uraninites, identification of Th, Nb, Ta, Sn, Be, Li, Zr, Hf, Ti, rare-earth elements (REE) minerals, investigations on degree of structural disordering in Nb-Ta minerals, X-ray crystallographic and substitutional solid solution studies, clay minerals, triclinicity of K-feldspar, metamict minerals and influence of the degree of metamictisation on uranium beneficiation, characterisation of leached residue, beneficiated, heat-treated products, metallurgical slags and other mineralogical studies. The results of mineralogical research are used for elucidating physicochemical conditions and geologic processes that prevailed during mineral formation.

**Keywords:** *X-Ray Diffraction, Atomic Minerals, Metamict, Oxidation Grade, Triclinicity, Structural Disordering.*

### 1. Introduction

The X-ray diffraction (XRD) finds wide-ranging applications in different types of researches. Common applications of XRD are (i) Crystal structure determination, (ii)

Phase identification and identification of unknowns, (iii) Quantitative phase analysis, (iv) Quality control in run of mine, (v) Characterisation of polycrystalline and epitaxial thin films, (vi) Textural and stress analysis, (vii) Measurements related to texture and orientation in metals and polymers, (viii) Measurement of thermal expansion, stability and phase diagrams under changing-temperature and changing-pressure conditions, (ix) Pharmaceuticals, (x) Biophysics, and (xi) Forensic science.

Mineralogical study plays a dominant role in addressing several geological issues like genesis of rocks, ores, minerals, mineral systems, tectonic settings and many more. Several laboratory techniques are routinely employed in performing this type of study. Notably, petrological study (Fig. 1), transmitted and reflected microscopy, scanning electron microscopy (SEM), electron probe microanalysis (EPMA), neutron activation analysis (NAA), automated SEM-EDS mineralogy (QEMSCAN), X-ray fluorescence (XRF), X-ray diffraction (XRD), laser induced breakdown spectroscopy (LIBS) and Raman spectroscopy play dominant role. More advanced analytical techniques are also used for mineralogical study. In this paper various applications of X-ray diffraction (XRD) technique, which is a non-destructive and physical analytical method, in mineralogical researches are briefly outlined.

## **2. Experimental**

### **2.1 Condition**

Crystalline solids in the form of powders, single crystals, sheets, foils or filters.

### **2.2 Amount**

Powder - Several hundred milligrams.

Single crystal - an un-cracked, un-twinned crystal of 0.1 to 0.5 mm on a side.

### **2.3 Sample Preparation**

Single crystal - mounting on a fiber or in a glass capillary.

Powder – Crushed solids to 200#.

## 2.4 Mineral Separation

Rock is aggregate of minerals (Fig. 1). To study each mineral, they need to be separated from the host rocks (Fig. 1) in solid/powder form. The steps involved in this process are outlined

below<sup>1-25</sup>.

The rock specimen (Fig. 1) is initially examined using ultra violet lamp for the presence of secondary uranyl minerals. If secondary uranium minerals are present, they would exhibit fluorescence. Such fluorescent minerals are extracted and taken up for XRD study. Discrete coloured grains (Fig. 1) are also scooped up and mounted separately and investigated. The remaining sample is crushed in between 85-100 microns size fraction as per nature of sample. The sieved grain sample and the powder sample are subjected to sequential separation using heavy liquid media.

For separation, commonly used liquids are Bromoform ( $\text{CHBr}_3$ ) and Methylene Iodide ( $\text{CH}_2\text{I}_2$ ). Bromoform has a specific gravity (SG) of 2.88 and those minerals with specific gravities  $<2.88$  would float in this media. Thus, gangue minerals such as quartz, feldspar, mica would separate out in this media. The bromo-heavies are further separated with the help of methylene iodide (MI).

The SG of methylene iodide (MI) being 3.31, minerals like biotite, apatite, tourmaline, hornblende and some pyroxenes, having SG between 2.88 and 3.31, will come in the light fraction. The MI heavy mineral fraction, comprising minerals of interest, is further separated using Isodynamic magnetic separator.

Thus, various minerals come at different magnetic field strengths, namely, ilmenite (0.2 amps), garnet (0.35 amps), xenotime (0.45 amps), monazite (0.6 amps), uraninite (0.95 amps) and zircon (non-magnetic fraction). Each fraction is then powdered to about 200#, diffracted and diffraction pattern so obtained is studied independently.

Another part of the crushed sample is also centrifuged using bromoform and MI. Various fractions so obtained are studied for mineral phases including clays. This procedure of separation is undertaken to enrich and isolate minerals occurring as discrete phases in minute/trace quantity.

Thus, for instance, say uraninite with concentration levels of 0.04 to 0.06% in a sample can be separated into a fraction with concentration levels reaching as high as 50% to 75% and in a few cases to as high as 95 % in the separated fraction. Accordingly, this combination of separation procedure helps in the concentration of these scarce minerals much above to detection limit.

Various separates obtained are powdered to about 200#. This powder is slowly poured in sample holder groove. After that sample is pressed with glass slide to obtain smooth diffracting surface. This sample-filled holder is mounted in slot within the XRD unit and diffracted.

### **2.5 Analysis Time**

The analysis time ranges from a few minutes to days depending on speed and nature of study. High-capacity X-ray generators and PSDs decrease analysis time. Contrasting this, poorly crystalline samples increase duration of analysis. Phase quantification requires more count time to attain statistical precision.

### **2.6 Instrument and Standard Used**

Siemens D-500 diffractometer was used in most of the studies. NIST supplied Silicon standard was used for checking data of interplanar spacings.

### **2.7 Operating Conditions**

The accelerating voltage was generally kept at 35 kV and tube current at 22 mA. The  $\text{CuK}\alpha$  radiation (1.5418 Å), monochromatised using curved graphite monochromator, was used for diffraction.

### **2.8 Mineral Identification Using Search Match Methods**

Diffraction pattern of various separates form set of inter planar spacings ( $d_{hkl}$ ). The  $d_{hkl}$  for all crystalline materials have been grouped by the International Center for Diffraction Data (formerly the Joint Committee on Powder Diffraction and Standards) using procedures helpful in their identification. The Fink and Hanawalt are the two well-known search match methods.

Certain isostructural minerals give a powder pattern that are undistinguishable on initial diffraction. Such minerals when subjected to heat-treatment convert to a

different form. The pattern of each of these heat-treated-product would be different depending on the composition of the initial mineral. As an example, fluorite, uraninite, pyrite and sphalerite are isostructural and give their respective reflections at the same angle. When these minerals are heated, they transform to their stable oxide phase whose powder patterns are different from one another, thus leading to their identification.

Minerals containing uranium and thorium as essential constituents are irradiated internally by alpha and beta particles and gamma radiation released during the radioactive decay. The alpha particle has the mass of a helium nuclei and moves in a recoiling trajectory. When the alpha particle encounters an atom, it dislocates the atom from its mean position. As a result, the mineral loses its crystallinity and becomes optically isotropic. This process is called metamictisation and the mineral is said to be metamict.

The original or the near original structure can be restored by heating the sample in a muffle furnace below the temperature of their phase transformation. Thus, the metamict mineral is heated in a series of steps starting from about 500<sup>0</sup> C onwards for a period ranging from 3 to 24 hours and examined each heat-treated fraction for restoration of their structure. In general, heating the sample would result in the restoration of its original structure.

## **2.9 Limitations**

### **2.9.1 General**

In XRD study, only crystalline phases can be identified. Overlapping of peaks may restrict mineral analysis and quantification. Nature of matrix also influences diffraction pattern. For example, strongly diffracting minerals may mask poorly diffracting phases. Preferred orientation, as exhibited by mica, increases intensity of diffracted beam, which limits quantitative phase analysis. Fluorescent material may enhance background of diffraction pattern. It may also cause saturation in low-capacity detectors.

### **2.9.2 Accuracy**

Quantitative study of powder mixtures with <1% accuracy and higher precision is achieved under favourable conditions with appropriate standards.

### **2.9.3 Sensitivity and Detection Limits.**

In practice, detection limit changes with the type of XRD unit. Whereas, in principle, the limiting factor is the given duration of analysis.

## **3. Results and Discussion**

### **3.1 Mineralogical Research**

The most common applications of XRD in mineralogical researches related to radioactive/atomic minerals are as follows<sup>1-31</sup>.

Identification of primary (uraninite, coffinite, brannerite, davidite) and a host of secondary uranium (uranyl phosphates, silicates, carbonates, vanadates, etc.) and other ore (and associated gangue) minerals in uranium ore deposits/occurrences. Due to the soft nature, flaky habit and fine-size nature, common occurrence as fillings, coating, encrustations, of secondary uranium minerals, XRD is of immense help in identifying such mineral phases, which otherwise pose severe problems in their identification by conventional optical mineralogical techniques.

Determination of the oxidation grade of polygenetic uraninites for elucidating genesis of uranium ores from diverse geological settings is done. This data is useful in distinguishing genetic aspects of uranium deposits formed in various geological settings, namely, Pegmatitic, Proterozoic unconformity-related, Metamorphic, Metasomatic, Metasediments, Sedimentary, French Veins, and Hydrothermal. Apart from these, prevalence of temperature (range) during formation of uranium deposits is also inferred. Characteristics of clay minerals hosted in diverse types of uranium ore deposits/occurrences also reveals about genesis of uranium deposits.

Identification of Th, Nb, Ta, Sn, Be, Li, Zr, Hf, Ti, rare-earth element (REE), and other associated ore and gangue mineral assemblages is routinely done. Investigations on degree of structural disordering in primary minerals of niobium and tantalum are

done to unravel the attendant physicochemical conditions during ore genesis. X-ray crystallographic and substitutional solid solution studies are performed, mainly on U, Th, Nb, Ta, Sn, Zr ore-minerals.

Determination of triclinicity of K-feldspar from rare-metal and rare-earth-mineralised granites and pegmatites is done to elucidate the evolutionary history of parent rocks and hosted mineralization. K-Feldspar cooled slowly under falling temperature in plutonic conditions will be reflected by maximum value of triclinicity (close to unity).

Fingerprinting of metamict minerals and investigations of influence on the degree of metamictisation on uranium beneficiation are done (Fig. 2). This study revealed that highly metamictised phases are more amenable for uranium leaching (Fig. 2). Characterisation of leached residue, beneficiated, and heat-treated products of uranium ores is also done (Fig. 2). Identification of metallurgical slags for mineral, heat-treated products and chemical phases are also routinely done.

Identification and structural study of atomic (monazite, rutile, zircon, ilmenite) and associated industrial (andalusite, sillimanite, garnet) minerals in beach sand and off-shore mineral deposits are performed. Several other mineralogical studies include determination of composition of olivine, garnet, feldspar, identification of new phases, and so on.

### **3.2. Complimentary Techniques**

Neutron diffraction is more suitable for location of light atoms in a crystal structure, whereas gamma-ray diffraction is useful for structural and defect studies of crystals. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) are additionally useful for mineral identification and quality control and on unraveling reactions in solid-state. X-ray fluorescence (XRF) gives compositional data, which helps in mineral identification<sup>26-</sup>

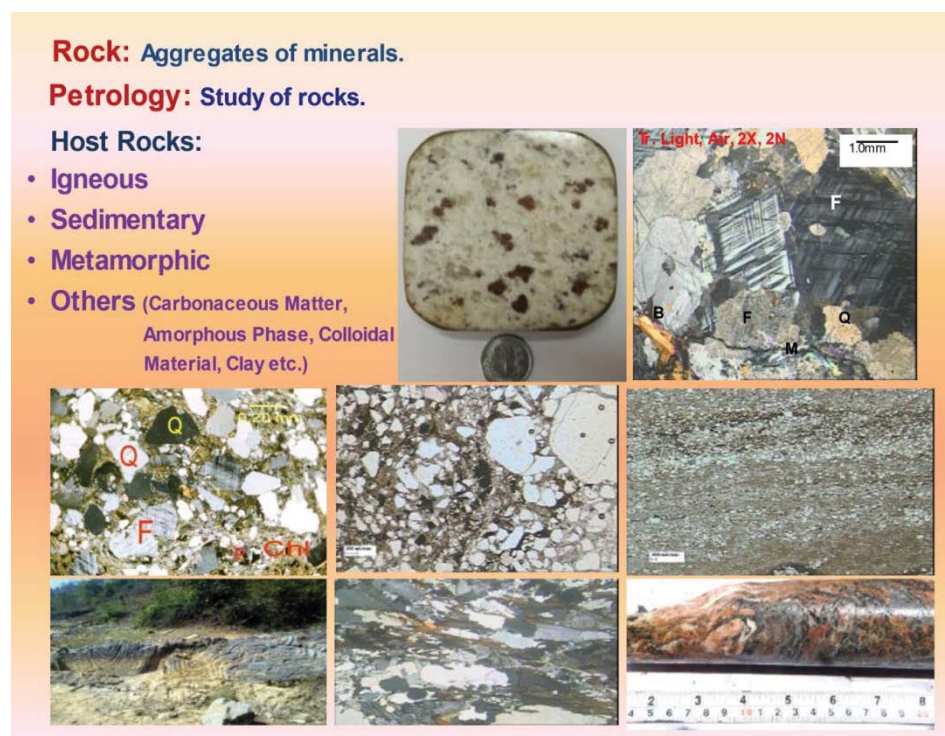
#### 4. Conclusion

The X-ray diffraction is a versatile nondestructive analytical technique and finds wide ranging applications in mineralogical research for elucidating physicochemical conditions and geologic processes that prevailed during mineral genesis.

#### 5. Acknowledgements

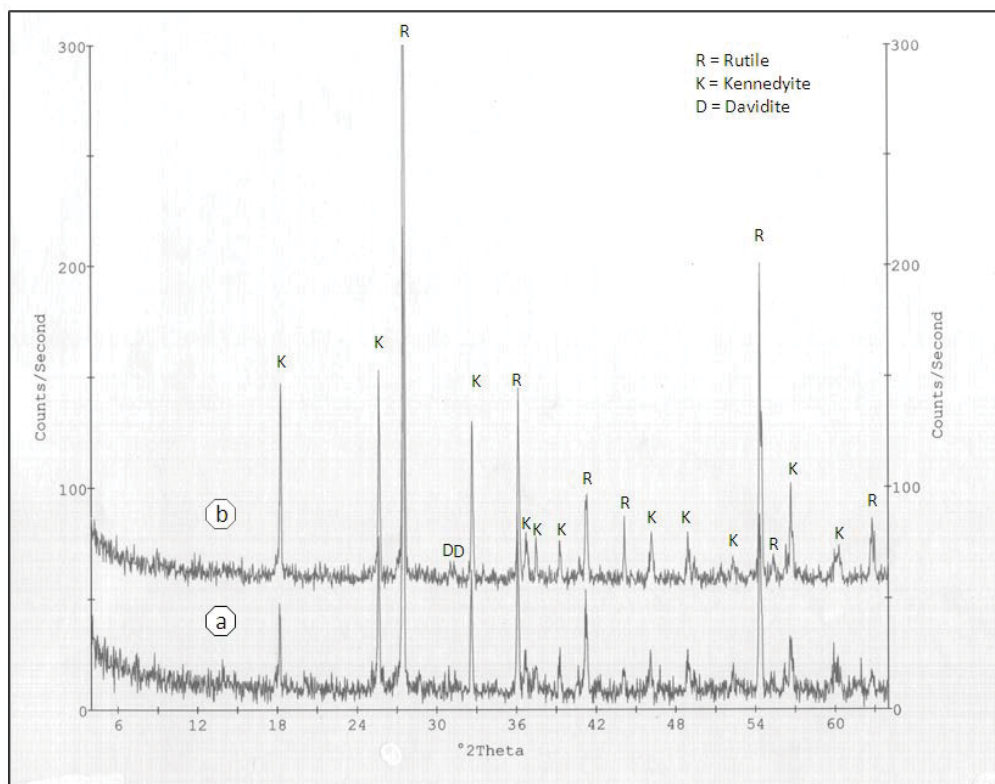
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#### Figures:



**Fig. 1.** Igneous, metamorphic and sedimentary rocks and other geological materials with their constituent mineral aggregates. Individual minerals are separated physically using heavy media liquids (bromoform and methylene iodide) and isodynamic magnetic separator from such mineral aggregates from samples of interest and studied independently using X-ray diffraction for various types of mineralogical researches. Q – Quartz, F – Feldspar, Chl – Chlorite, B – Biotite, M – Muscovite.





**Fig. 2.** X-ray powder pattern of successively heat-treated fractions of leached residue of feed ore from albitite belt, western India. Note only two minor reflections of davidite (marked D) and complete absence of brannerite. Also, note very prominent reflections of kennedyite (marked K) and rutile (marked R). Formation of kennedyite (K) and also additional (and hence enhancement of intensity of) rutile (R) is due to breaking and conversion of anatase in to another high-temperature polymorph of Ti on account of heat treatment.

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