

Article



# Polymetallic Uranium Mineralisation in Rohil, Rajasthan, Western India: Insights from Mode of Occurrences, Structural Controls, Alteration Geochemistry and Exploration

Ajoy Kumar Padhi<sup>1</sup>, Mrinal Kanti Mukherjee<sup>2,\*</sup>, Brajesh Kumar Tripathi<sup>3</sup>, Dheeraj Pande<sup>1</sup>, Balbir Singh Bisht<sup>1</sup> and Bhabesh Chandra Sarkar<sup>2</sup>

- <sup>1</sup> Atomic Minerals Directorate for Exploration & Research, Hyderabad 560004, India
- <sup>2</sup> Department of Applied Geology, Indian Institute of Technology (Indian School of Mines), Dhanbad 826004, India
- <sup>3</sup> Atomic Minerals Directorate for Exploration & Research, Jaipur 302030, India
- \* Correspondence: mrinal\_km67@yahoo.co.in

Abstract: Geological and radiometric studies of outcrops aided by extensive subsurface exploration through drill holes in an otherwise soil-covered terrain revealed the existence of low grades, medium tonnage, and metasomatite types of polymetallic uranium deposits at Rohil in India. Microscopic studies, electronprobe micro analyses, and geochemical analyses of samples from lodes indicate the polymetallic nature of mineralisation involving copper and molybdenum, in addition to uranium. Wide variations in the composition of fluid (S-, F-, P-, and O-rich) led to the formation of sulphides, fluorite, U-phosphosilicate, quartz, and magnetite, respectively, and are associated with uraninite. Litho-geochemical analyses from the Rohil deposit indicate multifarious metasomatic alterations associated with polymetallic mineralisation occurring in veins. The major mineralogical and metasomatic controls on rock compositions and the extent of material transfer processes that influenced the host rocks and mineralisati on are quantified by molar element ratio studies and alteration plots. General element ratio (GER) diagrams on chemical analyses of rock samples reveal albitisation and chloritisation as major and microclinisation, sericitisation, carbonatisation, and silicification as minor wall rock alterations associated with ore mineralisation. The alteration box plot between the chlorite-carbonate-pyrite index (CCPI) and the Ishikawa alteration index (AI) indicates the influence of hydrothermal activity and dominance of both albitisation and chloritisation. The ore zone is controlled by meso- and microstructures and the geometry of the soda- and potash-metasomatised zone around hydrothermal veins. This zone contains several anastomosing mineralised veins defined by a prominent joint that is set in quartzite that strikes subparallel to the axial surface of the  $F_2$ isoclinal folds and the pervasive schistosity S1 in the quartz-feldspar-biotite schist. Aventurisation of albite and microcline, established through electron probe micro analyses, can be considered as a pathfinder for uranium mineralisation. The close association of uranium and metallic sulphide mineralisation with microstructural, mineralogical (albitisation, chloritisation, and microclinisation), and geochemical variations can be applied as suitable exploration guides in a similar geological set-up worldwide.

Keywords: uranium; polymetallic; alteration; molar element ratio; CCPI; aventurisation; Rohil

# 1. Introduction

Global uranium deposits classified under the metasomatite type [1] consist of unevenly disseminated uranium in structurally deformed rocks that were affected by alkali metasomatism viz. sodium and/or potassium metasomatism [2] (Figure 1). Alkali-metasomatism refers to the geological process by which alkali (Na or K)-rich hydrothermal fluids interact with the country rocks and form the altered rocks mainly composed of albite or potassium feldspar and accompanied by additional alteration minerals [1–6].



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**Figure 1.** World map showing major metasomatite-type uranium deposits and the present study area (modified after [2])

While U-mineralisation, Na-metasomatism, and deformation are arguably related, the genesis is more complex and episodic in most of the deposits. Uranium mineralisation associated with Na-metasomatism varies in age from the lower Proterozoic to the Mesozoic. The host rocks also vary widely, from granite and tuff to metasediments and carbonates. In such deposits, the views on the relationship between alkali-metasomatism and uranium mineralisation differ significantly. While some of the researchers consider alkali-metasomatism at the syn-ore stage, others opine in favour of such an event prior to uranium mineralisation. Additionally, the roles of other alteration phenomena such as chloritisation, silicification, and sulphidisation have not been emphasised. The trace element geochemistry varies to a great extent due to wide variability in the composition of host rock and the mineralising fluid. Only a few of them such as Kirovograd, Ukraine [1,3], Valhalla, Australia [6], Michelin, Canada [7,8], Elkon [9], Lianshanguan, China [10,11], show copper and molybdenum concentration associated with uranium despite variation in the geochemistry of the host rocks. Uranium deposits in similar geological environments are reported in Lagoa Real [12,13], Aricheng, Guyana [14,15], Kitongo [16], Coles Hill, USA [1], Espinharas, Brazil [17], and Itataia [18] (Table 1).

Despite their worldwide occurrence (a total of 78 identified so far), they represent a significantly under-explored [1,2] type, and more research is needed to better understand the genesis of this type of deposit and to develop predictive exploration paradigms. The spatial relationship between uranium mineralisation and deformation structures in all metasomatite deposits is not well-documented [2,19]. Furthermore, the coexistence of other metals of economic importance in a deposit not only demands suitable beneficiation techniques, but also influences the valuation and mineral economics of the deposit.

The Atomic Minerals Directorate for Exploration and Research (AMD) of the Government of India has a proven mineral reserve of 8000 tons of uranium oxide with a low grade (0.062% U<sub>3</sub>O<sub>8</sub>) at Rohil [4,5]. Rohil (Lat.27°33′25″ N: Long. 75°29′25″ E) is located about 120 km NNW of Jaipur, the capital of Rajasthan, India. It is characterided by Na-metasomatite-type uranium mineralisation hosted in albitised metasediments of the mesoproterozoic Ajabgarh Group of the Delhi Supergroup [4,5,20]. In the study area, a structure-controlled, poly-metallic, low-grade medium tonnage uranium deposit is established through systematic subsurface exploration by AMD. The study of local geology around Rohil has so far been limited due to scanty exposures and mainly confined to the borehole core study during subsurface exploration. The nature of host rocks and subsurface exploration for uranium mineralisation have been discussed by several workers [5,21–24]. However, there are several gap areas related to deformation patterns based on data on mesoscopic structures, relationships, and the confinement of multimetallic mineralisation to the broad deformation zone. Various wall rock alteration features such as albitisation, chloritisation, silicification, and carbonatisation have been identified by earlier studies [4,21], but their significance as a guiding factor for exploration has not yet been established. The nature, composition, and physico-chemical parameters of the mineralising fluid need to be inferred. Mineralisation is largely associated with mild to moderately albitised metasediments. However, mineralisation also occurs in non-albitised zones with the presence of sulphides. The tectonic and fluid events in the Rohil deposit and their relationship with deformation and alteration events are uncertain. This is mainly due to the low grade and lensoid nature of the ore bodies and the complex structural evolution of the host rocks, which has hindered the identification of the morphology and mode of occurrence of the ore bodies in the field and at the hand specimen scale.

The geologic and geochemical features in micro-domains can replicate large-scale events [25]. In this paper, an attempt is made to (a) integrate structural data from the mesoscopic scale in surface exposures and borehole cores to microstructural observations to establish their contribution to mineralisation, (b) identify the alteration phenomena, preferably the prominent ones, to emphasise their contribution towards uranium mineralisation, (c) characterise the alteration phenomena and the possibility of identifying them as exploration guides, and (d) outline the paragenetic sequence of the ore minerals. The aim is to define the major mechanisms controlling the uranium, copper, and molybdenum occurrences so that the results should help in the development of more proficient exploration strategies for this deposit type in similar geological set-ups.

Deposit, Country, Resource in Kiloton U, Grade	Host Rocks (Rock Age)	Alteration Assemblage	Geochemistry	Formation Temp.	Ore Age (Ga)	References
Valhalla, Australia, 57, 0.07%	Mylonitised metabasalt and metasiltstone (Orosirian)	Early: albite, riebeckite, calcite Syn-U: apatite, zircon, brannerite Late: Uraninite, haematite, dolomite chlorite, coffinite, quartz, galena, pyrite, Cu-sulphides	Loss: Si (?), K, Ba, Rb Gain: Na, Ca, U, Zr, P, V, Y, Sr	340–380 °C Isotope geochem.	1.56-1.51	[6]
KirovoGrad, Ukraine, >250, 0.07%–0.15%	Gneiss, granite, iron-rich rocks (Archaean–Orosirian)	Stage 1: riebeckite/arfvedsonite, albite, carbonate, magnetite, apatite Stage 2: albite, apatite, pyrite, zircon, hematite, uraninite Late: aegirine, calcite, hematite, Late U: uraninite, coffinite, calcite, dolomite, biotite, Fe oxides, chlorite, Fe-Cu-Pb sulphides	Loss: Si Gain: Na, Ca, U, Zr, P, V, Y, Sr	Stage 1 and 2 alteration 300– 500 °C. Late alteration 150–200 °C	1.90–1.70	[1,19]
Novokonstantinovskoye, Ukraine, 93, 0.14%	Granite, minor gabbro and monzonite (Palaeoproterozoic)	Epidote-chlorite and chlorite-albitite, uraninite, brannerite, pitchblende, coffinite	Loss: Si Gain: Na, Fe, U, Ti		$1.808\pm0.027$	[1]
Krivoy Rog, Ukraine, 0.07%–0.2%	Metasediments (carbonate, quartzite, schist, banded iron formations) (Proterozoic)	Carbonate-alkaline metasomatism Chlorite, carbonate and haematite, davidite, nenadkevite, pitchblende, coffinite	Loss: Si Gain: Na, Mg, Fe, U		1.80-1.75	[19]
Elkon, Russia, <62, 0.05%–0.15%	Gneiss and migmatite, (Archaean– Palaeoproterozoic)	Stage 1: K metasomatism Stage 2: albite, sericite, adularia, illite, chlorite, haematite, pyrite, carbonate	Loss: Na, Al, Ca, Mg, Mn, P and Ti Gain: K, Fe, U, Au		0.135	[1]
Coles Hill, USA, 45, 0.054%	Deformed granite, augen gneiss, amphibolite	Na- metasomatism Albite, calcite, apatite, chlorite, haematite, sericite, zeolite.	Loss: Si Gain: Na, U, Fe, P, Ca		0.417	[1]
Lagoa Real, Brazil, 100, 0.12%	Mylonitised gneiss (large-scale ductile shear zone) Orosirian	Albite, pyroxene, garnet, uraninite, Zircon, allanite, carbonate	Loss: Si, K, Rb Gain: Na, Ca, Sr	$450\pm50\ ^{\circ}\mathrm{C}$ Initial phase	$1.87\pm0.07$	[13]
Michelin, Canada, 74, 0.07%–0.15%	Mylonitised metarhyolite, metavolcaniclastic rocks, metasediments, (Orosirian)	Quartz and K-feldspar with minor plagioclase, calcite, biotite, homblende, pyroxene, magnetite, hematite, traces of titanite, apatite, zircon	Loss: Si, K Gain: Na, U, Zr, Mo, W		$1.83\pm0.03$	[7,8]
Espinharas, Brazil, 8, 0.12%	Leucocratic granites and orthogneisses + mesocratic biotite-amphibole paragneisses	Albite, riebeckite, chlorite, calcite, coffinite, apatite, Ti-silicates, xenotime	Loss: Si, K, Rb, Sr Gain: Na, Ca, Fe, U, Th, Nb, Y, Pb	$500 \pm 50$ °C Intial phase	0.820 ± 0.01	[17]

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Deposit, Country, Resource in Kiloton U, Grade	Host Rocks (Rock Age)	Alteration Assemblage	Geochemistry	Formation Temp.	Ore Age (Ga)	References
Itataia, Brazil, 142, 0.19%	Epigenetic whereby the fluids are of magmatic, metamorphic, and meteoric origin	Sodic alteration and silica leaching. Amorphous apatite (collophane) formation	Loss: Si, Fe, Mn Gain: Na, Ca, P, U, F	250–200 °C; 50–130 °C	0.63	[18]
Kurupung, Aricheng Guyana, 60, 0.1%	Monzogranite, syenite, episyenite	Albite, carbonate, chlorite, hydrothermal zircon, uraninite, Ti-U oxides.	Loss: Si, Fe Gain: Na, Ti, U	250–350 °C (fluid incl.); 210–280 °C (chlorite geochem.)	$1.995 \pm 0.015$	[15]
Kitongo, Cameroon, <25, 0.09%	Granite	Two-stage albitisation, chlorite, calcite, apatite	Loss: K, Rb, Nb, Ba, Si Gain: Pb, Zn, Ga, Hf, Sr, Fe, Al, P, Zr, U, Na, Ca		0.590-0.613	[16]
Lianshanguan, China	Granite, migmatite (Archaean–Proterozoic)	Albite, sericite, fluorite, carbonate, pitchblende, coffinite, sulphides	Gain: Fe, Pb, Zn, Cu, U	280–350 ° C	1.894	[1,10]
Rohil, India, >8, 0.06%	Metasediments—quartz biotite schist, quartzite, amphibole quartzite, carbonaceous (graphitic) phyllite	Albite, chlorite, homblende, fluorite, uraninite, pyrite, chalcopyrite, pyrrhotite, molybdenite	Loss: Si, K (?) Gain: Fe, Na, Cu, Mo, Pb, Zn, Ni, Co	350–400 ° C (XRD study)	0.826	[21]

#### Table 1. Cont.

#### 2. Regional Geology

The Rohil polymetallic uranium deposit is a part of the Mesoproterozoic Delhi Supergroup of rocks. The Delhi Supergroup covers about 7% (21,850 km<sup>2</sup>) of the total area of Rajasthan and is grouped into the North Delhi Fold Belt (NDFB) and the South Delhi Fold Belt (SDFB), based on geological and tectonic settings [26]. The NDFB comprises Khetri, Alwar, and Lalasot Bayana sub-basins from west to east, exposing rocks of Mesoproterozoic Delhi Supergroup deposited in graben and half-graben structures. The study area forms a part of the NDFB where sheared metasediments of the Ajabgarh Group of the Delhi Supergroup act as the host rocks for mineralisation (Figure 2).

The regional geology of the NDFB has been extensively studied by various researchers [27–31]. The NNE-SSW trending widespread zone of albitisation covering approximately 170 km length along strike with 6–10 km width nearly follows the Khetri lineament in the northeast and the Kaliguman lineament in the southwest and is possibly an expression of an intracontinental rift zone [32].

Stratigraphically, the Delhi Supergroup is divided into three groups from oldest to youngest. The oldest is the Raialo Group (constituted of dominant carbonates and mafic volcanics), followed by the Alwar Group (composed of dominant arenaceous facie rocks with mafic volcanics), followed by the Ajabgarh Group (composed of dominant calcareous and argillaceous facies with mafic volcanics) [33]. Three phases of deformation ( $D_1$  to  $D_3$ ) have been reported in the Delhi Supergroup of rocks [34]. The first ( $D_1$ ) deformation produced first-generation folds  $(F_1)$  that are tight to isoclinal and inclined with an axial planar cleavage ( $S_1$ ). The second-generation folds ( $F_2$ ) arising out of  $D_2$  deformation are upright to inclined with shallow to moderate plunge due NNE [34,35] and crenulation cleavage ( $S_2$ ) that are axial planar to  $F_2$  folds.  $F_1$  and  $F_2$  are, in general, co-axial, thereby making the  $F_1$  and  $F_2$  fold axes parallel. The trend of the axial trace of folds strikes NNE-SSW with a steep dip. The third-generation folds (F<sub>3</sub>) resulting from D<sub>3</sub> deformation are broad open folds that have a WNW-ESE trend of the axial plane which has resulted in a broad swing in the strike of foliation planes. The thermal event accompanies a subsequent stage of rifting facilitated by hydrothermal solutions resulting in widespread metasomatic overprinting. Alkali metasomatism was more pronounced along prominent shear zones and deep-seated faults [36]. The lithic units have experienced two phases of metamorphism-M1 prograde (amphibolite facies) and M2 retrograde (green schist facies) during the deformation phases.  $M_1$  was coeval with the  $F_1$  and  $F_2$  phases of folding (1450 Ma), and M<sub>2</sub> was coeval with  $F_3$  folding (850–700 Ma) [37]. The monazite U-Pb dating suggests that the latest regional metamorphic phase took place at 975 Ma, which was soon overprinted by phase(s) of metasomatism at 900-850 Ma; the peak metamorphic temperature was estimated to be  $531 \pm 16 \ ^{\circ}C$  [31].



**Figure 2.** Geological map of part of the Khetri sub-basin of the North Delhi Fold Belt and the location of Rohil (modified after [22]).

# 3. Deposit Geology

3.1. Lithology

The study area is mainly covered with aeolian soil. Rock exposures are limited to a single ridge of deformed quartzite of 700 m in length and 100 m wide and are available for direct geological observation (Figure 3). The litho-units chiefly comprise metasedimentary rocks belonging to the Ajabgarh Group of the Mesoproterozoic age of the Delhi Supergroup, as envisaged from the borehole core study [4,5,21,22]. The host rocks of uranium mineralisation are medium-grade metamorphic rocks, represented by a quartz–feldspar–biotite schist (QFBS), a carbonaceous/graphite schist, quartzite, calc-silicate, and a quartz–amphibole schist.



Figure 3. Rohil exploration block showing borehole locations and the projection of ore lodes.

Schistose rocks consist of variable amounts of quartz, biotite, amphiboles, K-feldspar, plagioclase, and garnet. Variations in mineral assemblage suggest argillaceous precursor sediments from which these rocks were derived. A graphite schist is fine-grained, contains variable proportions of quartz, carbonaceous matter/graphite, and biotite, and the precursor rock possibly originated due to sub-marine volcanism. Usually, fine-grained pyrite is observed along the schistosity planes of the graphite schist. Calc-silicates are mainly composed of tremolite, wollastonite, plagioclase, calcite, biotite, and quartz. Quartzites contain in addition to quartz, variable proportions of sericite, plagioclase, amphiboles, and graphite. A part of the metasedimentary quartzite within the zone of deformation is mobilised and recrystallised, which constitutes a major part of the hillock. Amphibolites are composed of green hornblende that are un-foliated.

A subsurface geological map based on the lithological studies of borehole cores indicates conspicuous lithological variations in the area (Figure 4). The metasediments are complexly folded and sheared, and have varied degree of alteration features viz. albitisation-, chloritisation-, silicification-, and ferrugenisation-obscured host rock characteristics. Veins/reefs of quartz, calcite, pegmatite, albitite, and amphibolite (hornblendite) have intruded into all the litho-units. A geochronological study by Pandey et al. (2022) reveals the Pb-Pb isochron age in the uraninite of Rohil as  $826 \pm 9$  Ma and U-Pb, and the Concordia upper intercept age in uraninite is  $842 \pm 18$  Ma [38].



Figure 4. A subsurface geological map of the study area (based on the correlation of borehole intercepts).

# 3.2. Structure

The geology is discernible only to the surface manifestation of an isolated hillock of brecciated quartzite. The litho-unit shows rare compositional banding ( $S_0$  plane) in places, with an overall N-S trend. The contact between quartzite and the QFBS is sharp and sub-vertical along the schistosity plane ( $S_1$ ), indicating that the  $S_1$  plane is parallel to  $S_0$ . In places, thin bands of quartzite within the QFBS show an isoclinal fold ( $F_1$  coaxially refolded to  $F_2$ ) with sharp hinges (Figure 5a).

The crenulations on the  $S_1$  of the QFBS define  $S_2$  cleavage which is axial planar to  $F_2$ folds developed in the quartzite bands (Figure 5b,c). The QFBS shows steeply dipping foliations parallel to the  $F_2$  axial surfaces (Figure 5d). Intercalations of quartzite bands within the QFBS are tight to isoclinally folded with bedding  $(S_0)$ , and foliations  $(S_1 \text{ and } S_2)$ are strongly transposed (Figure 5e). The strong preferred orientation of elongated quartz grains parallel to the cleavage planes in quartzite indicates transposed  $S_1$  and  $S_2$  foliations (Figure 5f).  $D_3$  deformation has led to gentle to open folds ( $F_3$ ) with an EW-trending axial surface (Figure 5g). The rocks are affected by multiple sets of fracturing. Quartzite is heavily jointed at most places with the development of conjugate and non-conjugate fracture sets (Figure 5h). Quartzites are affected by E-W striking and steep southwarddipping faults with the development of breccia (Figure 5i). N-S striking and E-W striking fractures intersect at nearly  $90^{\circ}$  and are spaced differently, which are developed during  $D_2$  and  $D_3$  deformations, respectively (Figure 5j). The N-S fractures serve as avenues for hydrothermal fluid flow-bearing U-Cu-Mo mineralisation. N-S trending shear zones developed at the contact of quartzite and the QFBS have facilitated intense albitisation and chloritisation, which forms the locale for polymetallic mineralisation (Figure 5k,l).



Figure 5. Cont.



Figure 5. Cont.



**Figure 5.** Field observations. (a) Tight to isoclinals  $F_1$  folds refolded to  $F_2$  in quartzite bands housed within the schist, coin dia. 2.3 cm, vertical section orthogonal to fold axis, viewing south; (b) the development of crenulations on  $S_1$  of the QFBS that define crenulation cleavage; the cleavage is axial planar to  $F_2$  folds developed in the quartzite bands on bottom left part of the photograph, coin dia. 1 cm, vertical section orthogonal to fold axis, viewing south; (c) sketch of the crenulations with an enlarged view of the demarcated block in (b); (d) the QFBS showing strong foliations parallel to the pencil, steeply dipping towards SW ( $84^\circ \rightarrow 245^\circ$ ); this foliation is parallel to the  $F_2$  axial surfaces, vertical section viewing  $335^\circ$ ; (e) intercalations of quartzite bands with the QFBS that are strongly folded; bedding ( $S_0$ ), foliations ( $S_1$  and  $S_2$ ) are strongly parallel, vertical section orthogonal to strike of bedding and foliation, viewing south; (f) strong preferred orientation of elongated quartz grains parallel to the cleavage planes ( $S_1$  parallel to  $S_2$ ), vertical section normal to strike of the cleavage, viewing  $175^\circ$ ; (g)  $D_3$  deformation has led to gentle warping ( $F_3$ ) on thinly banded quartzite with an EW trending axial trace, plan view; (h) heavily jointed quartzites with the development of conjugate

shear fractures, vertical section viewing N350°; (i) fault breccias in quartzites, note the angular blocks of quartzites suspended within finer matrix of quartzite, viewing  $N350^{\circ}$ ; (j) fracture sets that occur on the quartzites intersect at nearly 90° and are spaced differently; the N-S fractures serve as avenues for hydrothermal fluid flow bearing U-Cu-Mo mineralisation; plan view; (k) patches (green) of copper mineralisation on vertical jointed surfaces in quartzites that extends N-S; coin dia. 1 cm, plan view; (I) radiation survey across the strike of the foliation in the QFBS, note the blue-green streaks of secondary copper mineralisation that are associated with uranium enrichment (159 ppm) when traced across the schistosity; (**m**) repetition of concentric laminae due to a folded axial surface ( $F_2$ folded by  $F_3$ ) in alternate bands of the QFBS and quartzites; (n) pyrite-pyrrhotite mineralisation along fractures within quartzite; (o) mineralised brecciated quartzite (albitisation absent); (p) a vein containing uranium and sulphides (mainly pyrite) and chlorite along fractures developed in earlier albite-rich rock; note a minor displacement of the vein along a fracture perpendicular to the vein  $(D_3 \text{ deformation});$  (**q**) albite-I, which is parallel to schistosity plane, has been cut across by fracture filled with albite-II; (r) drill core showing aventurisation (brown spots) on pink albitite; (s) drill core showing molybdenite (M) along microfractures in albitised quartzite. All the borehole cores are of NQ size.

In addition to surface signatures, borehole cores are studied in detail to understand the complexity of structure and its role in polymetallic ore mineralisation. Repetition of concentric compositional layering in the drill core within a gap of 1 m indicates that the borehole penetrated through fold hinges at high angles to the fold hinge line (Figure 5m). Quartzite is affected by fractures of variable dimensions, at places brecciated and filled dominantly with pyrite–pyrrhotite (Figure 5n,o). Uranium-bearing veins rich with sulphides and chlorite are confined along fractures developed in albite ( $Ab_1$ )-rich rock (Figure 5p). A minor displacement can be observed in the vein due to D<sub>3</sub> deformation in Figure 5p. Both generations of albite can be witnessed in tandem in borehole cores close to the mineralised zone. While  $Ab_1$  is dominantly parallel to the schistosity plane, later generation albite ( $Ab_2$ ) is mainly confined to or in close vicinity of microfractures (Figure 5q). Aventurisation is a noticeable phenomenon in drill cores as the borehole approaches intercepting mineralised zones. The brown spots developed on the pink albitites are due to a submicron-sized iron-rich phase leading to aventurisation (Figure 5r). Stringers of molybdenite (M) occur along microfractures in the borehole core of albitised quartzite (Figure 5s).

The overall structure of the quartzite ridge is of a southerly-plunging, overturned synform with an axial plane steeply dipping towards the west, which represents the  $F_2$  fold structure as a result of  $D_2$  deformation. The orientation of the fold axis (Figure 6a) is  $16^\circ \rightarrow 182^\circ$ .

The great circle passing through the plot of the trace of the fold axis on the map and the plunge of the fold axis in Figure 6a indicate the orientation of the axial plane of the  $F_2$ fold structure. The axial plane dips  $73.9^\circ \rightarrow 271^\circ$ . The  $F_2$  synform is further cross-folded into open upright folds with an axial plane striking east–west. The  $F_2$  hinge line is oriented N-S both at the northern and southern end of the ridge but takes a NE-SW trend at the centre of the ridge. The ridge has been affected by numerous joints with variable trends which are broadly grouped into six sets (Figure 6b). A set of joints that strikes sub-parallel to the axial surface of the  $F_2$  synform is hereby termed a J1 set of joints. These have a shallow dip with an orientation of  $25^\circ \rightarrow 100^\circ$  and have a spacing of 10–13 cm. J2 and J3 sets of joints are conjugate and strike parallel to the strike of the  $F_3$  fold axial surface along E-W. Similarly, J4 and J5 are a conjugate set of joints that strike NE-SW (Figure 6b). J6 is an isolated set of joints that strike NW-SE (Figure 6b).



**Figure 6.** Stereographic projection diagrams (equal area, lower hemisphere) for orientation data of structural elements from the study area. (a) A synoptic plot of  $S_0//S_1$  poles. The blue-filled square indicates the pole to the best-fit girdle to the  $S_0//S_1$  poles and, therefore, indicates the orientation of the fold axis ( $16.1^{\circ} \rightarrow 185.7^{\circ}$ ). The great circle indicates the orientation of the axial surface of the overturned  $F_2$  fold. (b) Plot of joint planes of sets J1–J6 and the axial plane of  $F_2$  fold ( $F_2$  AP).

# 3.3. Mineralisation and Its Mode of Occurrence

A radiometric survey using a hand-held scintillation counter reveals that the intrinsic uranium content is higher than the background along the eastern contact between quartzite and the QFBS. This zone showing a higher radiometric value can be traced for a varying width of 40–50 m with an overall trend of N15<sup>0</sup>E in the northeastern flank of the ridge, which indicates the trend of uranium mineralisation. Surface radiometric data obtained at every two-meter interval along the east–west profile line was plotted to show the distribution (Figure 7).



# Profile section across Rohil hill



The plotting of data of an elemental concentration was carried out along a transverse section line across the trend of one lode zone (Figure 8).



Figure 8. Elemental (U, Cu, and Mo) distribution and variation in concentration along the depth.

The elemental concentration of uranium, copper, and molybdenum show high variability with depth.

# 4. Analytical Methods and Observations

Borehole core samples from the mineralised zone and adjoining non-mineralised zone were collected for microscopic, EPMA, and geochemical analyses. The main objective was (i) to identify the role of microfractures on mineralisation, (ii) to categorise various alteration processes through quantification, and possibly (iii) to define the modes and generations of mineralisation.

## 4.1. Petrography

Petrographic analyses were performed on the altered host rocks within the zone of mineralisation using both transmitted and reflected light microscopy to identify the minerals and understand the texture, microstructure, and mineral paragenesis. Standard optical microscopy and electron probe micro analyses were carried out. The quartzite predominantly consists of medium- to coarse-grained, anhedral, and highly strained quartz. Fine-sized and strain-free quartz grains developed around grain margins of the strained quartz due to dynamic recrystallisation. The QFBS contains a variable proportion of quartz, K-felspar, and biotite as major constituents with local scale variants containing amphibole, garnet, and chlorite. The grain size varies from medium to very coarse in places. The veins and metasomatic effects are controlled by structure (shearing along the litho-contact). Composite veins are constituted of pyrite  $\pm$  pyrrhotite  $\pm$  chalcopyrite  $\pm$  molybdenite  $\pm$  Fe-oxide  $\pm$  ilmenite  $\pm$  uraninite. Gangue minerals in the composite veins are secondary quartz  $\pm$  chlorite  $\pm$  calcite  $\pm$  fluorite  $\pm$  epidote.

The contact between quartzite and the QFBS is sharp and the effect of flattening leading to the stretching of grains parallel to the plane of contact is evident (Figure 9a).

The contrast in rheological properties between layers of different compositions gives rise to a difference in response to stress. In the polymetallic complex mineralising fluid, the minerals of different elements crystallised according to their temperature of formation. Uraninite is the main uranium-bearing mineral in this polymetallic suite. Uraninite occurs as clusters and disseminations and is frequently associated with chalcopyrite, pyrrhotite, pyrite, molybdenite, and graphite occurring as vein-fill. The sharp grain boundary between uraninite and sulphides (pyrite, pyrrhotite, and chalcopyrite) indicates their co-genetic origin (Figure 9b,c). However, uraninite formed relatively earlier than the sulphides due to its higher temperature of crystallisation. At many places, chalcopyrite and pyrite form the girdle surrounding uraninite indicates their relative sequence of crystallisation from the same fluid. The role of microfractures (<10 to 50 µm width) in carrying the mineralising fluid is discernible (Figure 9b,d). Two sets of microfractures perpendicular to each other, one set filled with chalcopyrite, are formed earlier and have been truncated by the ones filled with pyrrhotite developed in the later episode of deformation (Figure 9e). Uraninite aggregate formed with limbs of protrusions at  $120^{\circ}$  from the apex of the triple junction containing melt [39], whereby the limbs might have developed due to forceful injection of a uranium-bearing fluid along a narrow microfracture (Figure 9f). The mineralised and nonmineralised meta-sedimentary rocks differ in the intensity of deformation and alteration.

#### 4.2. Electron Probe Microanalyses

Further study on microstructures is based on observations under an electron microprobe (CAMECA SX 100 model) at the EPMA laboratory, AMD, Hyderabad. Backscattered electron (BSE) images are captured using a 15 keV acceleration voltage and a 20 nA current with an image record time of 30 sec. The grain boundaries of uraninite vary from polygonal to seriate-interlobate as individual grains and occur in composite aggregates. Uraninite grains are euhedral to anhedral with size ranges of 0.03–0.8 mm and chalcopyrite is anhedral and ranges from 0.01 to 0.1 mm, whereas molybdenite is elongated, fibrous, and ranges in grain size from 0.02 to 0.8 mm. Pyrite is the most abundant among ore minerals, with variable shapes (euhedral to anhedral) and sizes (<1 micron size inclusion to >1 mm discrete grain).



Long fibers of molybdenite occur along parallel microfractures within the microcline (Figure 10a).

**Figure 9.** Photomicrographs. (**a**) Sharp contact between quartzite and the QFBS; the effect of shearing led to the stretching of grains parallel to the plane of contact; transmitted light (TL), under cross nicol(ucn); (**b**,**c**) the sharp grain boundary between uraninite and sulphides (pyrite, pyrrhotite, and chalcopyrite) indicate their co-genetic origin; (**d**) uraninite and pyrite along a vein, secondary chlorite envelope around uraninite in albite-rich groundmass under reflected light (RL), inset: same image under TL; (**e**) two sets of fractures; earlier fractures are filled by chalcopyrite (Cp), which are slightly truncated by later pyrrhotite (Po) veins; (**f**) uraninite aggregate formed with limbs of protrusions at 120° from the apex of the triple junction containing melt.



Figure 10. Cont.



**Figure 10.** BSE images. (a) Molybdenite (Mo) strands parallel to the fracture (dotted line) and albite (Ab<sub>2</sub>, dark grey), replacing K-felspar (Kf<sub>1</sub>, light grey) along the fracture showing sawtooth-shaped intergrowths; (b) the development of flexural slip folds on molybdenite strands due to D<sub>2</sub> deformation; (c) the oxidation of fractured pyrite (Py) to goethite (Goe) and the alteration of folded molybdenite (Mo), the altered portions of molybdenite marked as Mo(A) show a much lower brightness than the unaltered part; (d) elemental X-ray images of Mo-L $\alpha$  and Si-K $\alpha$  on the demarcated portion in figure (c) indicate variations in elemental concentrations of Mo within the molybdenite grains due to partial alteration by Si bearing fluid; (e) U-mineralisation along the fractured contact of the QFBS (top left) and quartzite (bottom right); note formation of secondary K-felspar (Kf<sub>2</sub>) and albite (Ab<sub>2</sub>) surrounding uraninite (U) grains; Ab<sub>2</sub> was also observed to replace Kf<sub>1</sub> of the QFBS; (f)

pyrite stringers along the microfractures developed parallel to the long axis of actinolite (Act) during  $D_2$  deformation, the formation of sphalerite (Sp) and sphene (Spe) towards the close of  $D_2$  deformation, the pyrite vein is perpendicular to schistosity and indicates its development during  $D_3$  deformation; (g) uraninite, chalcopyrite (Cp), and pyrite along the fracture within an albite-rich groundmass; (h) paragenetic sequence of galena (G)-Sp-Cp-Py inferred from sulphide assemblage; (i) the association of fluorite (F) with uraninite and chalcopyrite; note the presence of coffinite (Cof) along the grain boundary and microfractures within uraninite indicating their formation at a later stage; (j) U-Py and quartz (Q) as a vein; note the chloritisation of biotite (Bt); (k) uraninite girdled with chlorite (Ch), Fe-K clay and albite; (l) secondary uranium phosphate (Up) associated with pyrite, chlorite, and apatite (Ap); the section is perpendicular to the vein. (Scale bar: (a-d,h,j): 200 µm, (e,f): 500 µm, (g,i): 50 µm, (k): 20 µm, (l): 100 µm)

Due to soda metasomatism, albite has replaced some of the microcline grains on either side of some microfractures. The albitisation of K-feldspar is a pseudomorphic procedure that preserves the external dimensions and shape of the initial phase. The creation of secondary porosity during the replacement process is consequently caused by any variations in relative solubilities and molar volumes between the initial and product phases [40–44]. As a result, albite and the original microcline developed highly anisotropic, sawtooth-shaped intergrowths (Figure 10a). The freshly formed interfaces seem to be semicoherent and exhibit cracks along the reaction fronts that signify elastic strain [41]. The resulting textures and interfaces between microcline and albite observed in this research are strikingly similar to those observed in the experiment by Norberg et al. (2011), who opined that the system was trying to minimise elastic strain along the newly formed interfaces [41].

Molybdenite also occurs as strongly folded fibrous veinlets, indicating that they have originated syn-kinematically with the D<sub>2</sub> deformation (Figure 10b). The elongated grains of molybdenite show well-developed flexural slip folds (F<sub>2</sub>) with an overall isoclinal geometry. The presence of uraninite and magnetite with molybdenite is noted. The axial plane of the folds on the molybdenite strands is parallel to the overall trend of fractures (Figure 10b,c). The elemental X-ray images of Mo-L $\alpha$  and Si-K $\alpha$  on the demarcated portion in Figure 10c indicate variations in elemental concentrations of Mo within the molybdenite grains due to partial alteration by a Si-bearing fluid (Figure 10d).

Fracturing is observed both along and across the foliation direction. It is moderate to intense, and more than two sets of fractures cut across each other and are filled with monomineralic or polymetallic veins. A fracture develops along the contact of the QFBS with quartzite, which is a favourable site for U-mineralisation (Figure 10e). Secondary microcline (Kf<sub>2</sub>) and secondary albite (Ab<sub>2</sub>) surround uraninite grains, indicating their formation along with uraninite. In Figure 10f, pyrite stringers are observed along the microfractures developed parallel to the long axis of actinolite (S<sub>1</sub> schistosity plane) during D<sub>2</sub> deformation, whereas a pyrite vein perpendicular to schistosity indicates its development during D<sub>3</sub> deformation.

Uraninite, the major uranium-bearing mineral, is invariably associated with pyrite and chalcopyrite. These two minerals often occur along the grain boundaries of uraninite (Figure 10e,g,i,j), indicating their cogenetic nature. The BSE image (Figure 10h) shows a rare coexisting occurrence of four sulphide minerals engulfed in albite; a paragenetic sequence of galena  $\rightarrow$  sphalerite  $\rightarrow$  chalcopyrite  $\rightarrow$  pyrite is inferred from the assemblage. The association of fluorite with uraninite, pyrite, and chalcopyrite indicates an F- rich composition of mineralising fluid (Figure 10i). The presence of quartz along the vein containing uraninite indicates a silica-rich mineralising fluid (Figure 10j). The development of clay and chlorite is observed surrounding most of the uraninite grains (Figure 10i–k). At places, there is an indication of a phosphate-rich fluid, which resulted in the formation of secondary uranium phosphosilicate (Figure 10l). This U-bearing complex mineral is associated with pyrite and chlorite within the veins.

#### 4.3. Chemical Characterisation of Key Minerals by EPMA

Six representative samples were selected for metal sulphides, chlorite, and feldspar to understand the effect of various alteration phenomena associated with uranium mineralisation. The mineral chemistry of these phases was analysed by using EPMA (CAMECA SX 100 model) at AMD laboratory, Hyderabad, India. The instrument operated with a LaB6 electron gun source. The data acquisition and matrix corrections were performed by using built-in software.

Mineral compositions of grains of plagioclases, K-feldspars, and chlorites were determined at 15 KeV/10 nA, 15 KeV/40 nA, and 20 KeV/40 nA, respectively. The spot size was 1.5 µm and the counting time was set to 10 s. The following standards were employed for the determination of mineral composition: albite (for Na, Al, Si), orthoclase (K), MgO (Mg), CaSiO<sub>3</sub> (Ca), Fe<sub>2</sub>O<sub>3</sub> (Fe), MnSiO<sub>3</sub> (Mn), TiO<sub>2</sub> (Ti), and BaSO<sub>4</sub> (Ba) supplied by CAMECA. The X-ray lines and crystals (in brackets) Na-K $\alpha$ , Mg-K $\alpha$ , Al-K $\alpha$ , Si-K $\alpha$  (TAP), K-K $\alpha$ , Ca-K $\alpha$ , Ti-K $\alpha$ , Ba-L $\alpha$  (PET), and Fe-K $\alpha$ , Mn-K $\alpha$  (LIF) are used for the analyses. The analyses of chlorites were run on the chlorite geo-mode.

Point analyses of various sulphide phases were performed using a 20 keV accelerating voltage, 40 nA current, and a 1.5  $\mu$ m diameter electron beam. Standards used for analysis were pyrite (for S), chalcopyrite (Cu), galena (Pb), nickel metal (Ni), Fe<sub>2</sub>O<sub>3</sub> (Fe), cobalt metal (Co), sphalerite (Zn), InAs (As), Mo metal (Mo), and Ag<sub>2</sub>Te (Ag) supplied by CAMECA.

## A. Feldspars

Compositionally, plagioclases are mainly albite with minor oligoclase (Table 2). The Na<sub>2</sub>O content ranges from 8.66% to 11.35% (Avg. 10.26%, *n* = 12). The CaO and FeO vary between <0.01% and 1.02%, and <0.01% and 0.85%, respectively. The stoichiometric formula for albite is Na<sub>0.75-0.97</sub>K<sub>0.0-0.05</sub>Ca<sub>0.0-0.05</sub>Fe<sup>+2</sup><sub>0.0-0.03</sub>Al<sub>0.97-1.05</sub>Si<sub>2.95-3.05</sub>O<sub>8</sub>. The K<sub>2</sub>O content in K-feldspars ranges from 14.07% to 16.70% (Avg. 15.60%, *n* = 14). The Na<sub>2</sub>O, FeO, and BaO contents vary from 0.08% to 0.35%, 0.03%, and 1.29% to <0.01% to 1.13%, respectively. The stoichiometric formula for the K-feldspar is K<sub>0.90-0.97</sub>Na<sub>0.01-0.03</sub>Ba<sub>0.0-0.02</sub>Fe<sup>+2</sup><sub>0.0-0.05</sub>Al<sub>0.97-1.03</sub>Si<sub>2.97-3.03</sub>O<sub>8</sub>. K-feldspars are dominantly microcline, as per petrographic studies. The mineral chemistry signifies that feldspars in the study area fall on two ends of the Ab-Or-An ternary plot and are devoid of any intermediate products. Fe<sup>+2</sup> content, though small, is invariably present in all of the point analyses.

B. Chlorites

Biotite and actinolite in the host rocks are the precursors of chlorites. A chemical analysis of chlorite shows a wide variation in composition with 27.71%-35.43%SiO<sub>2</sub>, 14.44%-19.26%Al<sub>2</sub>O<sub>3</sub>, 11.38%-27.42% FeO, and 12.04%-21.25% MgO (Table 3). The FeO/MgO ratio shows a significant variation within a range of 0.72 to 2.38. A high FeO/MgO ratio of >2 is observed very close to the uraninite grains.

Albite														
Mol wt%	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	Min	Max
SiO <sub>2</sub>	68.6	69.28	68.23	67.61	68.54	66.24	69.11	67.66	67.71	68.29	71.24	71.49	67.61	71.49
TiO <sub>2</sub>	bdl	0.01	bdl	bdl	bdl	0.1	bdl	0.1						
$Al_2O_3$	19.32	19.8	18.87	19.51	20.57	19.78	18.89	19.34	19.14	18.65	19.52	20.01	18.65	20.57
FeO	0.02	0.06	bdl	0.23	0.05	0.85	0.21	0.03	0.03	0.06	0.38	0.07	bdl	0.85
MnO	0.04	bdl	0.05	0.02	0.02	0.02	0.07	0.14	0.05	0.01	0.06	0.03	bdl	0.14
MgO	0.01	bdl	bdl	0.01	0.03	0.52	bdl	bdl	0.01	0.01	0.02	bdl	bdl	0.52
CaO	bdl	0.01	0.02	0.13	1.02	0.23	0.19	0.22	0.27	0.14	0.23	0.27	bdl	1.02

Table 2. Mineral chemistry of feldspar in the polymetallic uranium deposit of Rohil.

						1	Albite							
Na <sub>2</sub> O	11.35	10.51	11.28	9.98	10.73	10.45	10.66	9.08	8.66	11.2	9.66	9.53	8.66	11.35
K <sub>2</sub> O	0.02	0.04	bdl	0.1	0.16	0.11	0.82	0.24	0.03	0.09	0.09	0.12	bdl	0.82
BaO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
	99.36	99.71	98.45	97.59	101.12	98.30	99.95	96.71	95.90	98.45	101.20	101.52	95.90	101.52
						Mi	crocline							
Mol wt%	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	Min	Max
SiO <sub>2</sub>	64.05	63.21	65.82	62.67	66.76	61.78	64.24	63.52	63.61	63.5	63.15	62.75	61.78	66.76
TiO <sub>2</sub>	bdl	0.03	0.01	0.02	0.08	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.08
Al <sub>2</sub> O <sub>3</sub>	17.64	17.7	18.03	18.47	18.21	18.19	17.78	17.54	17.29	17.48	17.14	17.47	17.14	18.47
FeO	0.34	1.29	0.1	0.61	0.23	0.36	0.13	0.19	0.08	0.04	0.16	0.03	0.03	1.29
MnO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.03	0.04	bdl	bdl	bdl	bdl	0.04
MgO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.03	bdl	bdl	bdl	0.03
CaO	bdl	0.04	bdl	0.05	bdl	0.07	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.07
Na <sub>2</sub> O	0.17	0.2	0.21	0.35	0.2	0.28	0.29	0.28	0.32	0.3	0.2	0.08	0.08	0.35
K <sub>2</sub> O	15.67	15.51	16.07	15.38	15.84	15.17	15.77	15.58	15.89	15.79	15.92	15.72	15.38	16.07
BaO	0.05	0.02	0.2	0.75	0.07	1.13	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.13
TOTAL	97.92	98.00	100.44	98.30	101.39	96.98	98.21	97.14	97.23	97.14	96.57	96.08	96.08	101.39

Table 2. Cont.

Table 3. Mineral chemistry of chlorite in the polymetallic uranium deposit of Rohil.

Mol wt%	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Min	Max
SiO2	32.60	34.79	32.44	29.77	31.97	32.44	35.43	28.10	29.64	28.53	28.24	29.29	30.81	28.92	29.01	28.29	27.97	27.70	27.71	35.43
TiO <sub>2</sub>	bdl	bdl	0.02	0.02	bdl	bdl	0.03	0.08	0.01	bdl	0.05	bdl	0.03	bdl	0.03	bdl	0.01	0.01	bdl	0.08
Al <sub>2</sub> O <sub>3</sub>	17.24	15.61	16.61	19.26	18.18	16.17	14.44	16.02	16.25	15.67	16.55	16.11	16.52	16.01	15.93	16.18	15.70	15.53	14.44	19.26
Cr <sub>2</sub> O <sub>3</sub>	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Fe <sub>2</sub> O <sub>3</sub>	2.85	4.71	3.44	2.02	3.38	2.80	4.42	0.55	1.03	0.65	0.83	1.05	2.25	1.08	0.88	0.80	1.37	0.95	0.55	4.71
FeO	14.56	13.13	14.98	18.38	16.60	13.77	11.38	24.56	20.54	25.09	23.76	20.73	19.35	22.97	24.36	24.15	27.42	26.65	11.38	27.42
MnO	0.19	0.14	0.14	0.13	0.13	0.18	0.13	0.29	0.23	0.19	0.29	0.25	0.09	0.30	0.23	0.17	0.31	0.35	0.09	0.35
MgO	21.02	18.91	19.12	18.52	17.99	21.12	21.25	15.95	18.61	15.89	15.86	18.02	17.58	16.38	16.29	15.79	12.04	13.21	12.04	21.25
CaO	0.34	0.84	0.50	0.15	0.22	0.49	0.78	0.09	0.11	0.09	0.14	0.14	0.21	0.07	0.08	0.08	0.18	0.14	0.07	0.84
Na <sub>2</sub> O	0.02	0.09	0.04	bdl	0.05	0.05	0.04	0.08	0.09	0.04	0.09	0.09	0.06	0.08	0.05	0.07	0.12	0.07	bdl	0.12
K2O	0.06	0.08	0.02	0.08	0.20	0.01	0.04	0.01	0.03	0.02	0.04	0.04	0.17	0.03	0.02	0.06	0.02	0.04	0.01	0.20
H <sub>2</sub> O*	12.15	12.08	11.87	11.86	11.98	11.93	12.16	11.12	11.49	11.15	11.18	11.35	11.60	11.22	11.30	11.12	10.81	10.80	10.80	12.16
Total	101.05	100.39	99.18	100.20	100.70	98.97	100.11	96.90	98.08	97.36	97.07	97.11	98.71	97.09	98.23	96.77	95.99	95.51	95.51	101.05
FeO/MgO	0.82	0.92	0.95	1.09	1.09	0.77	0.72	1.57	1.15	1.62	1.55	1.20	1.22	1.46	1.54	1.58	2.38	2.08	0.72	2.38

bdl: below detection limit.

# C. Sulphides

Pyrite and molybdenite are the predominant sulphide phases, followed by chalcopyrite, pyrrhotite, sphalerite, and minor galena (Table 4).

Two types of sphalerites are identified based on their Fe content. Type 1 contains 66.23%–67.86% Zn, 27.42%–28.44% S, and 0.58%–1.07% Fe (n = 3), whereas type 2 shows 60.04%–62.56% Zn, 29.45%–30.84% S, and 5.11%–6.27% Fe (n = 9). The wide variation in composition indicates their formation from different fluid compositions, or possibly, at different P-T conditions. A chalcopyrite analysis shows variation in composition with 31.92%–35.11% Cu, 31.43%–31.85% S, and 29.06%–30.62% Fe (n = 6). The mineral chemistry of molybdenite shows 55.40%–59.87% Mo and 34.57%–38.67% S (n = 6). The marginal fall in total weight percentage in pyrite, chalcopyrite, and molybdenite is attributed to the effect of alteration. The alteration effect on pyrite and molybdenite is discernible in BSE mode where the grains show a patchy appearance and a reduction in reflectance (Figure 10c). The partial alteration of some grains is possibly due to oxidation by the action of a silica-rich solution or meteoric water. However, galena and sphalerite grains seem to be unaffected, thus indicating that the oxidation of the sulphides took place at a moderately low temperature.

			C	halcopyr	ite			Molybdenite Molybdenite (Alt						te (Altere	ed)
Wt%	G1 *	G2	G3	G4	G5	G6	Avg	G1	G2	G3	Avg	G1	G2	G3	Avg
S	31.77	31.57	31.43	31.75	31.54	31.85	31.65	38.67	38.59	38.38	38.55	35.01	35.79	34.57	35.12
Fe	29.17	30.62	30.55	29.06	29.32	29.66	29.73	0.04	0.02	0.05	0.04	0.05	0.06	0.08	0.06
Со	0.04	0.09	0.23	< 0.01	< 0.01	< 0.01	0.06	< 0.01	< 0.01	0.03	0.03	< 0.01	< 0.01	< 0.01	< 0.01
Ni	0.01	0.11	0.18	< 0.01	0.01	< 0.01	0.05	< 0.01	0.02	< 0.01	0.02	0.01	< 0.01	0.02	0.02
Cu	34.72	32.20	31.92	34.74	34.68	35.11	33.89	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01
Zn	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05	0.03	< 0.01	0.04	< 0.01	0.01	0.02	0.01
As	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	0.02	< 0.01	0.01	< 0.01	< 0.01
Мо	0.60	0.63	0.66	0.63	0.65	0.54	0.62	59.33	59.87	59.85	59.68	56.22	56.09	55.40	55.90
Pb	0.13	0.19	0.18	0.08	0.12	0.04	0.12	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01
Total	96.44	95.41	95.14	96.26	96.31	97.20	96.13	98.12	98.57	98.32	98.34	91.46	91.98	90.14	91.19
		Spha	lerite			Galena			Ру	rite			Pyrrl	hotite	
Wt%	G1	G2	G3	Avg	G1	G2	Avg	G1	G2	G3	Avg	G1	G2	G3	Avg
S	28.44	27.73	27.42	27.86	12.15	12.10	12.12	50.10	49.21	49.32	45.96	36.67	36.25	36.48	36.47
Fe	0.71	1.07	0.58	0.79	0.26	0.10	0.18	43.52	46.10	43.61	41.90	59.01	58.98	58.72	58.90
Со	0.02	0.02	0.02	0.02	< 0.01	0.02	0.01	0.78	0.03	0.68	0.32	0.19	0.20	0.17	0.19
Ni	0.05	0.02	< 0.01	0.02	< 0.01	0.01	< 0.01	1.59	0.03	1.37	0.61	0.19	0.15	0.12	0.15
Cu	0.05	0.05	0.04	0.05	0.03	0.07	0.05	0.16	< 0.01	0.02	0.06	< 0.01	< 0.01	0.01	< 0.01
Zn	67.86	67.32	66.23	67.14	3.99	< 0.01	2.00	< 0.01	0.09	0.12	0.09	0.02	< 0.01	0.03	0.02
As	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.29	< 0.01	0.23	0.06	0.04	0.05	0.05
Мо	0.61	0.62	0.49	0.58	0.13	0.27	0.20	0.89	0.76	0.79	0.78	0.60	0.68	0.66	0.64
Ag	0.05	0.02	< 0.01	0.03	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Pb	0.06	0.05	0.24	0.12	85.21	85.61	85.41	0.38	0.02	0.48	0.23	< 0.01	0.08	0.14	0.07
Total	98.62	97.05	95.28	96.99	101.88	98.24	100.06	97.43	96.55	96.39	96.97	96.75	96.37	96.38	96.50

Table 4. Mineral chemistry of the sulphide phases in the polymetallic uranium deposit of Rohil.

\* G1, G2, G3, etc., are spots on the mineral grains for which analysis is obtained by EPMA.

#### 4.4. Whole Rock Geochemistry and Characterisation of Alteration

Alteration intensity is often described by qualitative terminology, such as weak–moderate–strong or incipient–patchy–pervasive. Of late, researchers have proposed quantitative tools based on elemental gain or loss for discriminating alteration intensity [42,45,46]. The tools can help with the characterisation of alteration and may suitably be utilised in future exploration [47].

A total of 69 borehole core samples from 10 boreholes from the zones of alteration associated with mineralisation were analysed for whole rock and trace element geochemical data at the chemistry laboratory of AMD (Table 5)

Estimations of uranium (as  $U_3O_8$ ) were carried out by Pellet fluorometer (ECIL, Model FL6224A, Hyderabad, India). Elements were analysed by an ICP-AES Sequence Spectrometer (Jobin Yvon, model ULTIMA2,France). Ferrous content was estimated using classical redox titrimetry using potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) as a titrant.

Oxides	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
SiO <sub>2</sub> %	57.86	69.78	60.76	58.35	66.36	53.10	51.10	60.12	57.38	45.75	54.27	38.91	38.05	49.05	53.02	49.15	52.95	59.44	67.14	39.21
TiO <sub>2</sub> %	0.88	0.72	0.44	0.85	0.58	0.64	0.50	0.48	0.26	0.74	0.81	0.59	0.50	0.69	0.66	0.51	0.47	0.50	0.43	0.55
Al <sub>2</sub> O <sub>3</sub> %	13.66	13.20	16.92	15.55	13.88	14.60	12.58	14.30	8.88	10.36	10.86	7.26	6.11	11.30	19.30	16.30	13.20	18.85	13.58	14.20
Fe <sub>2</sub> O <sub>3</sub> %	1.56	1.28	0.30	0.76	1.66	12.44	5.58	0.95	2.60	19.68	15.63	29.04	31.84	18.87	4.86	2.97	0.19	1.19	0.55	2.70
FeO %	7.80	2.90	4.38	3.58	1.98	3.45	4.56	6.58	1.75	3.96	2.67	4.70	4.76	3.17	5.75	10.19	16.17	6.32	3.31	8.62
MgO %	7.28	1.92	4.06	3.35	1.50	1.90	4.16	7.12	0.92	3.31	1.81	2.17	3.50	3.27	3.36	5.54	1.91	3.47	3.62	10.30
MnO %	0.06	0.06	0.04	0.04	0.06	0.02	0.14	0.06	0.06	0.01	0.01	0.01	0.02	0.02	0.04	0.04	0.01	0.02	0.05	0.07
CaO %	1.12	0.90	0.72	4.65	2.58	0.72	6.45	0.50	12.12	1.04	0.38	0.82	2.26	1.42	3.24	8.30	4.93	1.29	1.85	7.85
Na <sub>2</sub> O %	4.50	4.88	7.10	6.95	6.32	6.04	4.82	3.10	4.16	5.26	5.94	5.67	4.05	5.67	4.31	3.98	3.50	3.77	3.50	4.31
K2O %	0.06	1.54	0.06	0.06	0.10	0.06	0.14	2.38	0.05	1.20	1.56	1.32	0.48	1.56	2.29	0.60	0.54	2.29	1.45	0.25
P2O5 %	0.10	0.12	0.06	0.04	0.12	0.18	3.42	0.10	0.55	0.34	0.19	0.33	0.16	0.16	0.36	0.33	0.29	0.27	0.30	0.49
U <sub>3</sub> O <sub>8</sub> ppm	20	120	200	30	500	30	120	120	60	270	330	230	510	570	570	760	1400	10	640	770
U ppm	17	102	170	25	424	25	102	102	51	229	280	195	432	483	483	644	1187	8	543	653
Oxides	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
SiO <sub>2</sub> %	65.73	57.35	32.56	56.72	64.49	72.89	49.36	55.77	57.49	56.32	47.62	55.60	56.04	57.83	64.13	22.73	65.50	42.91	59.43	58.81
TiO <sub>2</sub> %	0.20	0.69	1.06	1.13	0.56	0.44	0.65	0.59	0.55	0.45	0.32	0.53	0.49	0.10	0.38	0.17	0.50	0.36	0.61	0.45
Al <sub>2</sub> O <sub>3</sub> %	13.91	12.04	7.98	13.02	10.21	8.38	10.34	21.66	17.89	19.96	16.15	21.04	20.20	16.81	19.01	12.06	21.68	16.38	17.65	18.78
Fe <sub>2</sub> O <sub>3</sub> %	0.24	3.24	0.32	0.32	3.86	4.83	14.04	1.60	8.46	4.34	11.09	2.66	3.87	0.79	0.20	18.81	0.23	8.11	0.16	0.65
FeO %	3.59	9.41	31.18	8.91	3.88	1.72	5.75	5.57	0.63	4.65	5.04	5.22	5.16	1.72	1.22	19.50	2.94	10.27	5.96	4.09
MgO %	4.11	2.58	5.35	4.50	28.00	1.16	3.65	3.16	3.38	2.08	1.10	2.86	2.29	0.45	0.29	2.54	1.60	8.35	5.73	4.94
MnO %	0.04	0.02	0.03	0.05	0.02	0.02	0.04	0.01	0.10	0.01	0.20	0.01	0.60	0.01	0.01	0.31	0.01	0.59	0.38	0.01
CaO %	2.17	1.10	6.29	2.82	0.67	1.32	1.70	0.67	0.57	0.57	1.02	0.63	0.06	8.46	4.71	1.99	1.64	0.47	2.82	6.22
Na <sub>2</sub> O %	3.17	4.85	2.43	4.45	3.50	3.50	3.64	3.50	2.83	4.04	4.58	2.97	4.99	8.08	7.80	1.61	3.37	1.61	3.35	3.32
K2O %	0.65	0.45	0.66	0.87	1.02	0.05	0.10	2.29	2.35	2.53	0.28	2.77	2.29	0.10	0.12	0.36	0.10	0.10	0.10	0.10
P2O5 %	0.25	0.19	0.24	0.27	0.19	0.10	0.23	0.05	0.06	0.05	0.11	0.10	0.11	0.01	0.04	0.08	0.03	0.04	0.02	0.04
U <sub>3</sub> O <sub>8</sub> ppm	220	2400	3940	1070	640	9390	820	10	120	120	1210	10	20	30	20	8100	60	1580	20	10
U ppm	187	2035	3341	907	543	7963	695	8	102	102	1026	8	17	25	17	6869	51	1340	17	8
Oxides	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
SiO <sub>2</sub> %	63.79	59.08	56.88	62.39	72.92	64.90	59.69	49.80	55.60	14.90	33.30	53.90	52.70	57.60	49.10	42.60	48.40	51.90	42.10	49.10
TiO <sub>2</sub> %	0.18	0.28	0.12	0.29	0.29	0.37	0.45	0.33	0.50	0.17	0.34	0.62	0.38	0.41	1.30	0.47	0.36	0.67	0.66	0.55

Table !	<b>5.</b> Cont.

Oxides	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Al <sub>2</sub> O <sub>3</sub> %	14.60	13.56	11.30	9.35	11.38	12.48	14.72	17.38	13.90	4.33	8.07	15.16	13.59	14.57	11.04	12.45	11.58	13.07	12.09	14.59
Fe2O3 %	2.55	2.69	9.75	6.18	2.37	4.85	2.17	10.81	12.46	52.73	33.30	9.60	10.74	6.86	16.36	20.07	19.85	12.28	20.34	15.31
FeO %	4.07	6.29	3.64	4.67	2.79	3.00	5.76	NA												
MgO %	3.00	5.02	3.18	4.01	0.22	1.24	1.54	4.37	3.24	0.42	2.78	7.15	5.09	3.34	3.33	3.70	1.65	5.03	3.22	6.98
MnO %	0.01	0.04	0.05	0.03	0.04	0.04	0.10	0.04	0.03	0.01	0.02	0.05	0.03	0.03	0.05	0.03	0.02	0.04	0.04	0.05
CaO %	0.71	2.59	2.78	2.55	0.49	1.40	2.51	1.74	2.10	2.32	1.96	1.86	4.45	4.33	5.61	2.37	5.01	4.51	1.98	1.44
Na <sub>2</sub> O %	5.43	2.62	1.13	3.09	4.78	4.51	6.08	8.45	6.70	2.88	4.39	5.50	7.61	8.42	7.28	6.99	6.79	7.19	6.41	5.53
K <sub>2</sub> O %	0.64	1.22	1.05	0.08	1.14	2.44	2.07	1.77	0.33	0.01	0.17	1.27	0.29	0.03	0.01	0.01	0.01	0.03	0.11	0.63
P2O5 %	0.14	0.54	0.09	0.14	0.10	0.17	0.65	0.15	0.12	0.01	0.03	0.12	0.12	0.11	0.01	0.08	0.10	0.01	0.24	0.12
U <sub>3</sub> O <sub>8</sub> ppm	10	60	930	2370	220	10	20	<10	<10	<10	<10	<10	<10	<10	<10	<10	990	7800	6550	310
U ppm	8	51	789	2010	187	8	17	<10	<10	<10	<10	<10	<10	<10	<10	<10	840	6614	5554	263

NA: not analysed in sample Nos. 48 to 69, total Fe oxide is not discriminated into FeO and Fe<sub>2</sub>O<sub>3</sub>.

#### 5. Discussion and Summary

Despite being of relatively low grade, metasomatite-type uranium deposits make up a sizeable part of the world's potential uranium supply. Similar characteristics are shared by the uranium mineralisation of the NDFB around Rohil and the albitite-hosted uranium deposits in Australia, Ukraine, Brazil, and Guyana. These deposits involve the transportation of uranium in a Na-dominated hydrothermal fluid and multiple stages of mineralisation.

Albite and microcline are found to be major rock-forming minerals in radioactive samples. Both types of feldspars are of more than one generation. Microcline (Kf<sub>1</sub>) is a common constituent in unaltered host rock (QFBS). Widespread albitisation (formation of Ab<sub>1</sub>) had taken place prior to ore mineralisation. The second-generation albite (Ab<sub>2</sub>) and K-feldspar (Kf<sub>2</sub>) associated with ore are the major alteration products. Although sodium metasomatism is more predominant, the effect of potash metasomatism cannot be ignored. BSE images reveal that the bright spots spread all over Ab<sub>1</sub> and Kf<sub>1</sub> are due to submicron-sized iron-rich phases within feldspar nanopores leading to aventurisation (Figure 11a,b). The textural relationships in both images indicate that these Fe-rich phases (that led to aventurisation) might have been derived from the same fluids that gave rise to uraninite–pyrite–chalcopyrite-bearing veins and penetrated the feldspars of the wall rocks in a close vicinity.

The elemental X-ray images (inset, Figure 11a) of Fe-K $\alpha$  and S-K $\alpha$  over a small area (white block in the figure) show the submicron size Fe-bearing particles (both oxides and sulphides) which are responsible for aventurisation. The textural study indicates that aventurisation postdates the first stage of albitisation and was probably contemporaneous with U-Cu mineralisation. Albitisation and K-metasomatism correspond to Na- and K-gains, respectively. The pre-ore stage feldspars (Kf<sub>1</sub> and Ab<sub>1</sub>) often have pitted appearance, micron-level inclusions, and discontinuous microfractures cutting across them. On the other hand, the feldspars in the ore stage (Ab<sub>2</sub> and Kf<sub>2</sub>) have a smooth texture, mainly occurring as veins by filling the fractures of variable width and length and at times, penetrating the host rock minerals in the direction perpendicular to the trend of the fracture. The replacement of primary K-feldspar (microcline, Kf<sub>1</sub>) by albite could have been due to alkali ion exchange between fluid and feldspar phases by a replacement reaction, such as:

Norberg et al. (2011) [41] opined that during such a reaction, about an 8% reduction in volume can take place due to the difference in the molar volume of K-Feldspar (109.1 cm<sup>3</sup>/mol) and albite (100.2 cm<sup>3</sup>/mol). This replacement leads to a reduction in all lattice parameters within the Si/Al-framework structure, resulting in reaction-induced porosity. This secondary porosity has been assumed to be three-dimensionally interconnected (Figures 9f and 10a), forming a network that facilitated fluid flow [40,41].

Albites (both  $Ab_1$  and  $Ab_2$ ) replace microcline (Kf<sub>1</sub>) along and also in close vicinity to microfractures (Figure 11b). The coexistence of pure albite with Na-poor K-feldspar and their lack of zonation suggests that, within a single sample and during the various stages of albitisation, local equilibrium was attained at least between these two feldspars. The continuity in the circulation of alkali-bearing fluids resulted in the replacement of the original K-feldspar by albite through a metasomatic process driven by differences in the equilibrium fluid composition [44].



**Figure 11.** BSE and elemental X-ray images showing various alteration phenomena. (**a**) Aventurisation of albite in close vicinity of veins containing polymetallic minerals, Fe Ka, and S Ka X-ray images (inset) indicate the presence of Fe minerals (oxide and sulphide) within nanopores of albite; (**b**) albite (Ab<sub>2</sub>, dark grey) replaces microcline (Kf<sub>1</sub>, light grey) along and also in close vicinity of microfractures; note the pitted appearance of Kf<sub>1</sub> due to the replacement by Ab<sub>2</sub> at the micron level leading to reaction-induced porosity; (**c**) biotite is altered to chlorite and K-feldspar, pyrite is altered to goethite; (**d**) elemental X-ray images of K-K $\alpha$  showing the occurrence of Kf<sub>2</sub> as small veins filling the void spaces and also as isolated grains; (**e**) elemental X-ray image of Fe-K $\alpha$  indicating the formation of a chlorite vein parallel to the Kf<sub>2</sub> vein. Uraninite (U), biotite (Bt), chlorite (Ch), pyrite (Py), and goethite (Go); (**f**,**g**) the occurrence of Kf<sub>2</sub> and Ab<sub>2</sub> in tandem in close vicinity to uraninite. Textural relationship between Kf<sub>2</sub> micro-grains and partially altered biotite provides evidence of the formation of Kf<sub>2</sub> at the expense of biotite; (**h**) part (rectangular box) of the BSE image in Figure 10e; K-feldspar (Kf<sub>2</sub>), albite (Ab<sub>2</sub>), and quartz (Q) constitute part of the vein along the interstitial space between uraninite (U) grain boundaries; (**i**–**k**) elemental X-ray images of Na-K $\alpha$ , K-K $\alpha$ , and U-M $\alpha$  of (**h**) for substantiation of the above observation. (Scale size: (**a**,**f**,**h**–**k**): 100 µm, (**b**–**e**) and (g): 200 µm).

The alteration of biotite is a retrograde reaction leading to the formation of chlorite and K-feldspar, as per the following equation suggested by Holness, 2003 [44]:

# Biotite + $H_2O \rightarrow Chlorite + K$ -feldspar

Thus, the secondary K-feldspar (Kf<sub>2</sub>) is formed both from the release of K during albitisation and due to the alteration of biotite (Figure 11c). Kf<sub>2</sub> occurs as small veins filling the void spaces and also as isolated grains, as envisaged from the elemental X-ray images of K-K $\alpha$  (Figure 11d). An elemental X-ray image of Fe-K $\alpha$  indicates the formation of a chlorite vein parallel to the Kf<sub>2</sub> vein (Figure 11e). Figure 11f indicates the occurrence of Kf<sub>2</sub> and Ab<sub>2</sub> in tandem in close proximity to uraninite. The textural relationship between Kf micro-grains and partially altered biotite provides evidence of the formation of Kf<sub>2</sub> at the expense of biotite (Figure 11f,g). Figure 11h is a part of the BSE image in Figure 10e. The elemental X-ray images of Na-K $\alpha$ , K-K $\alpha$ , and U-M $\alpha$  of the portion of the sample in Figure 11h reveal the formation of Ab<sub>2</sub> and Kf<sub>2</sub> along the interstitial space between uraninite grains (Figure 11i–k). Hence, the formation of Ab<sub>2</sub> and Kf<sub>2</sub> is co-genetic to uranium mineralisation. Holness (2003) suggested that during the circulation of alkalibearing fluids in a temperature gradient, feldspars become enriched in Na and K in the high- and low-temperature zones, respectively. Hence, the fluid flow direction in Figure 11h can be inferred to be from the top to the bottom of the figure.

Chlorite often forms rings around uraninite grains (Figures10j,k and 11c). It also occurs in the close vicinity of uraninite–chalcopyrite–pyrite assemblages (Figures 10i and 11f,g). At places, chlorite appears to replace pyrite at the uraninite grain boundary. There are possibly different types of chlorites having variations in mineral chemistry and morphology. A detailed study on the mode and role of chlorite formation is necessary.

The samples were litho-geochemically assessed using general element ratio (GER) diagrams [6,48] and an alteration box plot [45]. GER analysis was employed to quantify the material transfer of elements between the host rocks and the hydrothermal fluids [48,49].

Depending on the abundance of any mineral species, the samples 'trend' towards or away from mineral nodes in these diagrams. Because the GER diagrams exhibit compositional variations that are proportional to the additions and losses of elements experienced by rocks during material transfer, quantitative and proportional estimates of mineral modes (including hydrothermal alteration mineral modes) can be determined. These ensure proper recognition of different alteration styles and accurate quantification of the extent of alteration.

In the diagram of (Na + K)/Al vs. Na/Al, the data points fall along the line joining the albite node to the muscovite node but move towards chlorite mode (Figure 12a).

This is supported by a higher concentration of chlorite than muscovite in petrographic and EPMA studies. It also indicates the predominance of albite among feldspars. The K/Al versus Na/Al plot in Figure 12b supports observations of a sample cluster around the albite node [6]. Some samples trend towards the chlorite node from the albite node, indicating the presence of chlorite in these mineralised samples. The diagram also indicates a reasonable amount of K within the system. The (Na + K)/Al vs. (Fe + Mg)/Al plot indicates the trend of chloritisation (Figure 12c). Chlorite was added to the system due to the breakdown of other minerals (biotite and amphiboles) during deformation and alteration.

Uranium vs. Na/Al does not show any specific trend, indicating that though uranium mineralisation is associated with Na-metasomatism, U does not proportionately increase with Na content in the rock. This observation is substantiated by the plot of U in Figure 11d against the degree of albitisation expressed as K–(Na + Ca) [14]. When plotted against Fe/Al, U concentration shows an increase within a broad zone (Figure 11e). This signifies that the addition of Fe content within the altered rock corresponds to an increase in U concentration. Hydrothermal activity that led to the addition of sulphides (pyrite, pyrrhotite, chalcopyrite), contributes greatly to enhancing the Fe content in the altered zone. Additionally, there is a relative increase in Fe content due to the alteration of biotite to



Figure 12. Cont.





Figure 12. Cont.





**Figure 12.** (**a**–**f**) GER (molar ratio) diagrams. The blue line indicates K-gain and the red line is K-loss. Nodes of albite (A), K-feldspar (K), chlorite (C), muscovite (M), and biotite (B) are shown; (**a**) (Na + K)/Al vs. Na/Al, indicating predominance of albite when compared to chlorite; (**b**) Na/Al vs. K/Al diagram; (**c**) (Na + K)/Al vs. (Fe + Mg)/Al, showing the trend of chloritisation; no sample is fully devoid of Na and K; (**d**) the degree of albitisation diagram of K-(Na + Ca)/Al vs. U does not

show any definite correlation; (e) a diagram of Fe/Al vs. U, showing moderate correlation in some samples; (f) a diagram of (2Ca + Na + K)/Al vs. K/Al, showing trends of the mass transfer processes [50,51]; (g) an alteration box plot showing the dominance of albitisation and chloritisation as major alteration assemblages associated with uranium mineralisation [45]; (h) a graph of  $(K_2O + CaO)/Na_2O vs. TiO_2/FeO$  (tot), describing the dominant styles of hydrothermal alteration [52]; (i) MgO/Al\_2O\_3 versus K\_2O/Al\_2O\_3 molar ratio plots, indicating mineralisation associated with low-Mg chlorites [46]; (j) the QP diagram, indicating Na metasomatism [53,54]; (k) the alteration discrimination diagram [55]. The scaling of the symbols represents the concentration of uranium in ppm.

Alteration indices quantified by the concentration of selected mobile elements can relate to the precursor mineral or the alteration mineral of interest. These indices are gaining importance among exploration geologists [42]. The K-Na  $\pm$  Ca mass changes can be quantified by an alteration box plot [45], where the Ishikawa alteration index (AI = 100 × [MgO + K<sub>2</sub>O]/[MgO + K<sub>2</sub>O + Na<sub>2</sub>O + CaO]) is plotted against the chlorite–carbonate–pyrite index (CCPI = 100[MgO + FeO]/[MgO + FeO + Na<sub>2</sub>O + K<sub>2</sub>O]). In the present study, the plot reveals the dominance of both albitisation and chloritisation as major alteration phenomena (Figure 12g). The observation is substantiated by the graph of (K<sub>2</sub>O + CaO)/Na<sub>2</sub>O vs. TiO<sub>2</sub>/FeO (tot) proposed by Vonopartis et al., 2020, describing the predominant styles of hydrothermal alteration (Figure 12h) [52]. However, these diagrams have limitations in discriminating the chlorites on the basis of MgO-FeO content. To address this, MgO/Al<sub>2</sub>O<sub>3</sub> versus the K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> molar ratio plot is attempted [46]. The plot indicates the association of mineralisation with low Mg chlorites (Figure 12i). The Q and P parameters in the classification scheme [53,54] are defined as:

$$P = K - (Na + Ca)$$
 and  $Q = Si/3 - (K + Na + 2Ca/3)$ 

where P discriminates between K-feldspar and/or biotite (high P-values) and albite (low P-values). The Q parameter estimates the quartz content of a rock [54]. Albitisation is evident from the Q-P diagram (Figure 12j). The discrimination diagram proposed by Montreuil et al. (2013) [55] shows the predominance of albitisation and chloritisation (Figure 12k).

Unlike other Na-metasomatite uranium deposits, there is no complete removal of K and Si from the mineralised zone in Rohil. These elements formed their own minerals (K-feldspar and quartz) very near the place of their release. This leads to the prevalence of K-metasomatism as the third major alteration phenomenon in Rohil.

## 5.1. Controls on Polymetallic Mineralisation

The salient observations in the present study can be summarised to emphasise the controlling factors that influenced the deposition and concentration of U-Cu-Mo minerals.

## 5.1.1. Structural Control

The mineralised veins have been emplaced along the contact ( $S_0$  plane) between the quartzite and the QFBS, and along joints (J1) that strike approximately sub-parallel to the axial surface of the Rohil synform (Figure 6b). The conjugate joint sets J2–J3 and J4–J5 are relatively younger and devoid of mineralised veins.  $S_0$  at the contact between the QFBS and quartzite are subvertical to very steeply dipping towards SW. In addition to the  $S_0$  plane and J1 joints,  $S_1$  foliation in quartzite and the QFBS also acted as avenues for ore-bearing fluids. Additionally, it has already been stated that mineralisation distinctly occurs along microfractures, as has been seen in borehole cores and under the microscope. The contrast in rheological properties between layers of different compositions gives rise to a difference in response to stress during deformation. This could result in the formation of dilational zones at the litho-contact, which then can attract fluid flow. In the study area, polymetallic mineralisation is more concentrated at the contact of quartzite and the QFBS. While quartzite shows brittle deformation, the schistose rock underwent ductile to

brittle deformation. Additionally, mineralising fluid had relatively easier access within the schist due to higher permeability, whereas in quartzite, it is confined to secondary porosity developed due to the fracture system.

# 5.1.2. Na-K-Metasomatism

The close association of the ore zones and the metasomatically altered rocks indicate that the fluids responsible for the metasomatic changes were also the principal agents of epigenetic polymetallic mineralisation. The U and Fe-Cu-Mo ore within the zones of intense metasomatism are attributed to the influx and prolonged circulation of a complex fluid. Albitisation, chloritic alteration, and the formation of calcite, fluorite, and sphene are the principal mineralogical changes induced by the circulating fluid, which destroyed the pre-existing planar and linear structures of the rocks. These changes involve the removal of K and Si and the addition of Na, Ca, Ti, and F. Further, these changes and the associated ore deposition process may be related to two or more influxes of fluid complexes at separate intervals, or a single but prolonged phase of fluid circulation.

Uranium is introduced after pervasive first-phase albitisation of the host rock and is spatially and temporally associated with micro-fracturing of the albite-rich zone. These albiterich zones are significantly more permeable than the host rocks due to the development of secondary porosity through chemical dissolution. Uranium mineralisation is related to second phase albite (Ab<sub>2</sub>); the role of this soda metasomatism has been highlighted by earlier research based on petrographic studies. However, the present study reveals that the role of K-metasomatism is also quite significant. K-feldspars also occur in two generations; the first phase (Kf<sub>1</sub>), chiefly microcline, is inherent to the metasediments prior to hydrothermal activity. A significant part of these microcline grains is replaced by first-generation albite (Ab<sub>1</sub>). Albitisation of the first-phase microcline released K into the system. The second phase of K-feldspars ( $Kf_2$ ) is formed as a part of the alteration of biotite to chlorite. The released Si and K during the alteration of biotite and soda metasomatism have not been removed from the system but rather resulted in secondary K-feldspars and quartz. Thus, the paragenetic sequence of events among feldspars is ideally  $Kf_1 \rightarrow Ab_1 \rightarrow Ab_2$  and  $Kf_2$ . Therefore,  $Kf_2$ and Ab<sub>2</sub> are co-genetic with uranium mineralisation. However, U does not proportionately increase with Na or K content in the rock.

# 5.1.3. Episodic Hydrothermal Activity

The composition of fluid associated with uranium mineralisation shows wide variations (S-, F-, P-, and O-rich), leading to the formation of sulphides, fluorite, U-phosphosilicate, quartz, and magnetite, respectively.

- a. The majority of uraninites are rimmed by pyrite and other sulphides. Uranyl ions must have been carried by sulphur-rich fluids, the latter forming later-stage sulphides.
- b. In some domains, uraninite is in proximity to fluorite (Figure 10i). Hence, uranium might have been transported as uranyl–fluoride complexes from which uraninite and fluorite might have crystallised [1].
- c. Coffinitisation of uraninite along the fractures (Figure 10i) is indicative of the action of Si-rich fluids during the post-ore stage.
- d. Uranium phosphosilicate (Figure 10l) is a complex mineral that requires the presence of U-, P-, and Si- in the fluid phase within the system at the time of crystallisation.
- e. The presence of magnetite (Figure 10b) and quartz (Figure 10j) in juxtaposition to uraninite along veins is indicative of an O-rich fluid in the system at some point in time.

Thus, there is sufficient evidence of a variation in fluid composition that carried uranium in the labile state within the system, which is indicative of episodic hydrothermal activity.

# 5.2. Indications of Polymetallic Mineralisation

# 5.2.1. Aventurisation

Based on colour, there are three types of feldspars: white, pink, and reddish. Mineral chemistry reveals Fe-content (though minor) in both the feldspars, which probably is the reason behind their pink colouration. The reddish color is attributed to the presence of fine-grained Fe-bearing inclusions in nanopores in soda and potash feldspar-rich rocks, which are ascribed as aventurisation, leading to a spotty appearance (even very dark red spots) in places. The reddish ones often look dusty, dull, and baked. Field observations and petrographical studies reveal that the white and light pink types show low radioactivity and mineralisation, whereas the dusty reddish ones show relatively high radioactivity. A similar signature is also reported by Wilde, 2013 and Saleh et al., 2018 [20,56]. Aventurisation associated with albitised gneissic rocks has been reported in Ladera, Rajasthan [57]. Aventurisation has taken place during the main ore stage. It has affected the pre-ore stage albite  $(Ab_1)$  and microcline  $(Kf_1)$ . The BSE image and the corresponding elemental X-ray images in Figure 11a,b reveal that the major contributor to the aventurisation is the micronsize inclusions of iron within the nanopores of Ab1 and Kf1. The X-ray images indicate that some of these iron micro-particles are in the sulphide phase; however, the sizes of these particles are too small to analyse their mineral chemistry.

This phenomenon is visible on surface exposures and also along the borehole cores as we approach the uranium mineralisation zone. Albitisation is a regional phenomenon in NDFB, but aventurisation is restricted to the albites close to the mineralisation zone. Hence, such features on the surface can be future targets for subsurface exploration.

#### 5.2.2. Chloritisation and Sulphide Concentration

Chlorite is formed from the dissociation of biotite; however, a variety of chlorite is also formed around uraninite grains, which indicates its role in the precipitation of uranium from the solution (Figures 5p, 9d, 10i,k and 11c). The mineral chemistry of chlorite near uraninite shows a higher Fe/Mg ratio (>2). The authors opined a more detailed study on the nature of chlorite and its role in mineralisation process.

Broadly, two separate paragenetic associations of sulphides can be inferred: an earlier stratiform pyrite–pyrrhotite association partly mobilised during the regional metamorphism and the deformation of the Delhi Orogeny, and a late fluid-driven epigenetic molybdenite–uraninite–chalcopyrite–pyrrhotite–pyrite association with minor sphalerite and galena (Table 6). Uranium is generally mobilised in oxidised fluids and concentrated where fluid mixing brings about changes favouring the deposition of U-bearing minerals and associated metals [55,58]. The textural studies indicate that uraninite grains are invariably associated with pyrite, though the reverse is not always true. Rather, there is a better probability of finding chalcopyrite and molybdenite with uraninite.

Phases	Minerals	Pre-Ore Stage	Ore Stage	Post-Ore Stage
	Ilmenite			
	Titanite			
Ouidaa	Sphene			
Oxides	Magnetite			
	Uraninite			
	Goethite			
	Pyrite			
	Pyrrhotite			
Sulphidee	Molybdenite			
Sulpilides	Chalcopyrite			_
	Galena			
	Sphalerite			
Others				
Otners	U phosphate			

Table 6. A paragenetic sequence of ore minerals inferred from their textural relationships.

Dashed line represent episodic mineralization.

Thus, the permeable cataclasitic zones, the dilational parts of the fold and fracture systems (flexures and junctions), and mechanical heterogeneities (differences in permeability due to rheological contrast) at the litho-contact of quartzite with the QFBS are the favourable sites. The deformations generated weak planes through which Na-rich fluid could migrate and produce replacement-type albitisation. This regional scale albitisation might have created a more weakened rock with higher secondary porosity, which is susceptible to easier migration of mineralising fluids in later stages. The aventurisation of feldspars and the presence of chalcopyrite and molybdenite can be considered exploration guides.

#### 5.3. A Comparative Study of Rohil with Global Examples of Metasomatite Uranium Deposits

Metasomatite-type uranium deposits are confined to Precambrian shields affected by tectonic-magmatic activity and intense Na-metasomatism or K-metasomatism, which produced albitised or illitised facies along deeply rooted fault systems [1]. The principal uranium phases are uraninite, brannerite, and coffinite. The reserves are usually medium to large, but the grade is low (<0.2%U). Ukraine hosts the largest number of metosomatite-type uranium deposits. These deposits are developed within a variety of basement rocks, including granites, migmatites, gneisses, and ferruginous quartzites, which produce albitites, aegirinites, and alkali-amphibolics, as well as carbonate and ferruginous rocks. Relatively smaller deposits occur in the Elkon District (Russia), Itataia, Espinharas and Lagoa Real (Brazil), Valhalla (Australia), Kurupung (Guyana), Coles Hill (US), Lianshanguan (China), and Michelin (Canada). The Rohil deposit is relatively small both in tonnage and grade as compared to global uranium deposits (Figure 13).



**Figure 13.** Global metasomatite-type uranium deposits vis-s-vis global events in geological history. Uranium deposits proliferated during the Columbia supercontinent assembly during the Palaeoproterozoic period and waned during the Rhodinia breakup in the Neoproterozoic period and again started to proliferate during the Gondwana supercontinent assembly post-Pan-African Orogeny. The Rohil polymetallic uranium deposit represents the waning peak of the mineralisation episode in terms of both tonnage and grade.

While host rocks vary to a large extent both in composition and age, the association with shear zones and Na-K metasomatism are the common features. The alteration may result from various processes such as the interaction of magmatic fluids exsolved from a peralkaline granite, such as at Bokan Mountain, Alaska, to lower temperature basinal brine, as proposed for the Valhalla uranium deposit, Australia [6], or fluids with seawater composition, such as at Lagoa Real [12]. In most of these deposits, albitites form discontinuous occur over several tens of kilometers and individual Na-metasomatic zones are several hundred meters long [58]. Rohil falls within the NNE-SSW trending widespread zone of albitisation covering approximately 170 km in length and 6–10 km in width and is, therefore, comparable to the above.

As envisaged in Figure 13, metasomatite-type uranium mineralisation took place in three different episodes. The metallogenic epoch between 1.5 and 2.0 Ga is the most dominant one since all large deposits in Ukraine, Brazil, Canada, and Australia were formed during this period. Few other deposits, including Rohil, fall within the period of 0.6 to 0.85 Ga. Brittle deformation during the Neoproterozoic period, i.e., 850–700 Ma [1,37], facilitated the development of micro-fractures and brecciation leading to the formation of mineralised veins in Rohil. These deposits are relatively smaller in size and grade, except Itataia. The Itataia uranium deposit and other uranium occurrences in the African counterpart are likely part of the same mineralising event that occurred in the transition between the Cambrian and Ordovician periods. Cuney et al. (2009) and Veríssimo et al. (2016) suggest that the uranium mineralisation episodes associated with Na metasomatism occurred during the Brasiliano/Pan-African event (~500 Ma) [18,58]. Although all uranium deposits of this type are confined to albitite zones, not all albitites are uranium-bearing. Hence, the presence of these metasomatites is not the only prerequisite for uranium ore deposition. Other important ore-controlling factors are large, permeable cataclastic zones, dilational parts of fold and fault systems (flexures and junctions), and mechanical heterogeneities [1].

## 6. Conclusions

Polymetallic mineralisation in Rohil has been studied in terms of structural geometry, mineralising fluids, alteration geochemistry, and their controls on mineralisation. Structural analyses from the mesoscopic to microscopic scale along the deformed zone are used to constrain the timing of deformation and mineralising fluid events and establish the relationship between them.

The following can be summarised:

- I. The reaction-induced porosity and sawtooth-shaped intergrowths were developed during the alteration of microcline to albite, forming a network of microfractures that enables pervasive fluid flow.
- II. Polymetallic mineralisation is structurally controlled and extends dominantly along the fractures that are parallel to the F<sub>2</sub> axial surfaces. Mineralisation is syn- to post-kinematic and located along the N-S structural grain.
- III. Alteration diagrams substantiate the dominance of both albitisation and chloritisation as major phenomena and microclinisation as supportive wall-rock alterations.
- IV. Aventurisation of albite and microcline on the surface and subsurface can be helpful in prioritising future exploration targets for uranium mineralisation.
- V. An episodic variation (S-, F-, O-, and P-rich) in a hydrothermal fluid composition is established. The fluids responsible for alteration were also the principal carriers of epigenetic polymetallic mineralisation.

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