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A Study of Influence Factor on Uranium Fixation in the Tono Uranium Deposit, Japan

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堆積岩中のウラン濃集に係わる影響因子の研究(*)
—東濃ウラン鉱床を例にして—

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要　旨

東濃ウラン鉱床は、日本最大の砂岩型ウラン鉱床である。その成因は、鉱床分布地域の基盤花崗岩中のウランが、地下水によって溶出／運搬され、基盤花崗岩を覆う第三紀堆積岩中に濃集されたものと考えられている。これまでの地質学的及び地球化学的研究により、東濃ウラン鉱床中のウランは、強還元環境下での難透水帯中に黄鉄鉱や黒雲母、あるいは炭化した植物繊維と密接に係わって産することが認められている。

本論文では、このような特性を持つ鉱床中でのウラン濃集に係わる影響因子を評価するために、ウラン(U-233) を用いた雰囲気制御下でのバッチ式収着試験とトランジェントパルス法及び定水位法による透水試験を実施し、堆積岩の持つ化学的・構造的要因によってもたらされる核種保持性能についての考察を行った。

その結果として；

①化学的核種保持力による影響よりも、地質構造による地下水の透水性がウランの濃集に強く影響を及ぼしていると考えられること

②ウランの濃集値が、ウラン濃集の母岩である第三紀堆積岩のウラン保持能力を示している可能性のあること

③堆積岩中では、砕屑物である鉱物粒間とそれらの鉱物中の微小割れ目が、ウランの移行経路及び濃集場所として重要な役割を果たしていること

が示された。

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A STUDY OF INFLUENCE FACTOR ON URANIUM FIXATION IN THE TONO URANIUM DEPOSIT, JAPAN

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Key Words:Natural uranium/ Sedimentary rock / Pore structure / Hydraulic conductivity / Sorption partition coefficient(Rd)

SUMMARY

The Tono uranium deposit is the largest uranium mineralization situated in central Japan. The source of the mineralization is uranium which has been leached from the basement granite and transported by groundwater. It was then adsorbed and/or precipitated under reducing conditions established by the lignite rich sedimentary rock.

Macroscopic and microscopic studies have revealed that the uranium is concentrated in or around the pore spaces partly as coffinite or pitchblende closely related to pyrite, altered biotite and coaly plant tissues. It has become evident from hydrogeological and geochemical investigations that the zone in which uranium mineralization occurs has extremely low hydraulic conductivity and reducing condition.

The results of U-233 batch sorption experiments under controlled atmosphere and macro/microscopic observations can be useful for assessing the migration behaviour of nuclides in sedimentary rock.

1 INTRODUCTION

The geosphere acts as a massive physical and chemical buffer for nuclide migration. It controls the geochemical fluxes dominated by the rates of water movement. Nuclides will be anisotropically transported due to physical features such as sedimentlogical/petrological inhomogenities and structures of flow paths. Geochemical environment along the path will affect to retard the rate of movement of individual radionuclides. The studies of concentration mechanism of natural uranium in sedimentary rock can be applied to assess such influential processes for developing a migration model[1,2]. The present paper discusses the migration behaviour anticipated in sedimentary rock according to the results of macro/microscopic observations and the experiments.

In order to identify the most important nuclides retardation process of sedimentary rock, the Tono uranium sandstone type deposit has been investigated and the following studies were carried out.

(1)The macroscopic and microscopic occurrence of natural uranium has been investigated by radioactive logging, petrological observation and chemical analysis.

(2)For the characterization of microscopic occurrence and correlation between pore structure and uranium concentration, alpha autoradiography and electron probe microanalysis(EPMA) were used.

(3)Hydraulic conductivities of the high uranium zone were measured to assess the hydrological influence on uranium concentration.

(4)The sorption experiments using U-233 as a tracer were also carried out in order to estimate sorption value which will be able to assist to interprete the retardation and fixation capability of natural uranium in sedimentary rock.

2 GEOLOGICAL AND EXPERIMENTAL STUDY

2.1 Description of the Tono uranium deposit

The Tono uranium deposit is a sandstone type deposit present in the Tertiary Mizunami Group sedimentary rocks and is about 20 million years old(Figure 1)[3]. The uranium deposit occurs in the Toki lignite bearing Formation, which is considered to have been deposited as fluviatile or lacustrine sediments overlying unconformably the Toki uranium rich granitic basement. The Toki granite intruded into Paleozoic sedimentary rocks in the upper Cretaceous to Paleogene period. The Mizunami Group sedimentary rocks, composed of conglomerate or permeable sandstone and tuffaceous rock, are widely distributed along a palaeoriver-channel structure. Detrital materials, such as lignite, organic matter and secondary minerals (e.g. pyrite) are inevitably present and lignite and pyrite may have caused reducing conditions favorable for uranium precipitation and adsorption. The total uranium ore is distributed in an area of several hundreds meter width by 2-3km length with 10-30m thickness. The ore body is situated under unconfined groundwater, at 100 to 160 meters below ground level[4,5].

2.2 Characterization of uranium embedded zone

In order to characterize the uranium embedded zone, a borehole was made from the old mining gallery situated 130 meters below ground level. The borehole was investigated by radioactive logging to clarify the uranium distribution(Figure 2), and the following analysis were carried out thereafter.

a)Microscopic analysis

The purpose of this analysis is (1)to identify the differences of chemical compositions between the rock of uranium mineralized and of unmineralized zone, and (2)to find the preferential micro pore structure responsible for natural uranium migration in sedimentary rock. Bulk compositions and total uranium contents are measured by a conventional wet chemical analysis, colorimetry or fluorometry methods. The structure of pores have been examined using the alpha autoradiography. Alpha particle emission from natural uranium series nuclides of rock thin section was recorded in CR-39 plastic[6,7]. Examination was made using a stereomicroscope to obtain the initial matching of the etched detector with the section, thereafter transfering to a petrological microscope for detailed study and phase recognition. Use was also made of EPMA in confirming mineral identification.

b)Groundwater analysis

The redox potential and chemical composition of groundwater are important factors controlling the solubility and aqueous speciation of nuclides. The groundwater has been analysed in order to specify the characteristics of groundwater in the ore body zone. Groundwater was directly sampled from the borehole using double packer system installed at the location of high uranium zone. The collected groundwater is maintained under nitrogen atmosphere, and then immediately transferred to the laboratory to measure the chemical compositions. On the other hand, the geochemical parameters of groundwater, such as pH, Eh, electric conductivity have been measured in-situ by developed monitoring system[8].

Table 1 shows the characteristics of groundwater extracted from the ore body zone situated at 155 meters below ground level. These data has been obtained for over one year. Two

notable characteristics are recognized. Firstly, the groundwater is strongly reducing (Eh=-300 to -350mV measured by Pt and Au electrode) and slightly alkaline (pH=8.7 to 9.5). Secondary, the geochemical composition of groundwater is Na^+-HCO_3^- type and the uranium content ranges from 0.05 to 0.20ppb[9]. The geochemical modelling using PHREEQE code indicates that the groundwater is almost saturated with uraninite (Saturation index(SI)=-0.17) or coffinite (SI=-0.70), the dominant species is $U(OH)_4(aq)$ and the redox condition is controlled by siderite(SI=0.14) or pyrite(SI=1.65). It implies that this reducing condition is quite suitable for uranium(IV) mineralization.

c)Measurement of hydraulic conductivity

In order to clarify the geometrical features and hydrological influence on uranium concentration, hydraulic conductivities of uranium embedded zone were measured. Hydraulic conductivity will probably directly affect the mass of natural uranium which is dissolved and transported by groundwater. Two measurement methods were used to examine the core sample of hand specimen size from uranium embedded zone. One is the Constant Pressure Method(CPM) and the another is the Transient Pulse Method(TPM). The later method is originally developed by PNC[10]. In both the methods, triaxial compressive system is set up to reestablish the in-situ stress condition.

2.3 Batch sorption study

Two well petrologically analysed rock samples were selected from the mineralized and the unmineralized zone of core specimen for the U-233 sorption experiments. These representative rock samples are located in the tuffaceous sandstone closely adjoining

each other within the similar hydro-geochemical environment(Figure.3). The direct purpose of this sorption experiment is to estimate the chemical retention capability of sediments which have expected on inhomogeneous concentration of uranium during geological timescale.

Batch sorption experiments are carried out in a glove-box with a nitrogen atmosphere. The oxygen contents is less than 100ppm. The ratio of tuffaceous sandstone to groundwater is 19.6/50.0 and the contact time intervals are from 1 to 60 days. Dissolved U-233 in dilute nitric acid was added in groundwater. Mineral composition of both samples are also analysed by XRD. Major mineral phases and uranium contents are shown in Table 2. Mineralogy is quite similar except for the existence of smectite in the unmineralized rock sample. Solutions were sequencially separated by 0.45um filtration and ultrafiltration(10.000MWCO) in order to identify the colloid and colloidal substances. Solution concentration of U-233 was measured by alpha-spectrometry. Experimental conditions are shown in Table 3.

3 RESULTS AND DISCUSSION

3.1 Uranium distribution and its geometrical relationship on uranium embedded zone

The result of radioactive logging data shows that the uranium is quite inhomogeneously concentrated within the uranium embedded zone(Figure 2). The uranium contents is apparently different even among the sediments with quite similar mineralogy. Detail analysis of uranium contents shown in figure 3 indicates that the high uranium was concentrated in the relatively coarse

grained facies of tuffaceous sandstone. On the other hand, uranium contents of compacted fine tuffaceous sandstone is almost similar to the value of background.

Hydraulic conductivity measurement shows that the permeability of uranium embedded zone were extremely low(Figure 2). The measurement data varies the orders between 10^{-8} and 10^{-11} cm/s. The hydraulic conductivity of the coarse tuffaceous sandstone is relatively higher than the compacted fine tuffaceous sandstone. The largest difference of permeability between coarse and fine tuffaceous sandstone is almost three orders of magnitude. In such low order of permeable condition of the compacted tuffaceous sandstone zone, migration will probably be forced by mainly diffusion[11]. The hydraulic conductivity of the mineralized and the unmineralized zone which was selected as representative points for the batch sorption samples were quarried out $5.4X10^{-8}$ cm/s and $4.84X10^{-11}$ cm/s respectively(Figure 3). Those gaps might be gained also due to the differences of feature on sedimentary rocks between the mineralized and the unmineralized zone.

The data suggest close correlation between the structual features in this sedimentary rock, the hydraulic conductivity and the concentration of natural uranium. Especially, the difference of three orders of magnitude of hydraulic conductivity between the mineralized and the unmineralized zone implies that the uranium was dominantly concentrated in the permeable geological media. Hence, inhomogeneous concentration of uranium probably shows the different mass of uranium which has been transported by groundwater during geological timescale.

3.2 Migration behaviour of naturally occurring uranium in tuffaceous sandstone

Microscopic occurrence of natural uranium in sedimentary rock will be closely related to the structure of pores or transport paths formed after sedimentation. Autoradiographs of the alpha emission from thin sections of the mineralized rock show high concentrations of uranium in or around the spaces between detrital grains such as quartz, feldspar and lithic fragments. The space was also partly filled with altered biotite, clay minerals and fine organic matter(Figure 4). These voids will readily be assessed to spacially interconnect each other. It implies that the voids have probably functioned as preferential paths for natural uranium migration. It is also necessary to consider that the filling materials in the pore spaces could have functioned as a chemical and/or physical retardant[7]. On the contrary, microscopic observation of the unmineralized fine grained tuffaceous sandstone shows that the pore which is smaller than that of the mineralized rock is sporadically distributed and disinterconnected each other. The differences of such pore structure between the mineralized and the unmineralized rock will clearly show that the path structure strictly influences on nuclides transport and uranium concentration.

Microscopic study of alpha autoradiography and EPMA indicates remarkable associations between uranium and pyrite or iron oxide minerals(Figure 5). Framboidal and micro subhedral pyrite almost inevitably associate with high concentration of uranium partly observed as coffinite and pitchblende[12]. However, almost no concentration was observed in the pore spaces without pyrite or other iron oxide minerals. These associations indicate that the uranium concentration and fixation processes have close relationship with mineralogical phase dominating redox condition. Probably these minerals established strong reducing condition

in or around the pore and the flow paths. This reducing condition might readily caused the reduction of uranium from uranium(VI) to uranium(IV) and precipitated locally in the pore or flow path.

Microscopic migration behaviour in the pore or path will therefore be summarized that the pore or path structure controls the transported mass of uranium, and geochemical reaction will generate high uranium concentration thereafter.

3.3 Role of sorption on uranium concentration

Sorption partition coefficients(Rd) derived from batch experiments will be regarded as the retention capability for uranium(VI). Because the atmospheric condition of batch experiment was slightly oxidized. Therefore, these results may not directly indicate the acutual chemical retention capability which can be expected in situ under reducing condition. However, the Rd of mineralized and unmineralized rock, at least, will suggest the relative sorption capability for uranium.

Results from the U-233 batch experiments are given in Table 4. Rd of U-233 on the mineralized and the unmineralized rocks are 3 to 5 ml/g and 60 - 160 ml/g, respectively. It clearly shows that the unmineralized rock has 20 to 30 times greater degree of retention capability than the mineralized rock. In spite of the quite similar experimental conditions of both samples, the Rd of the both samples are quite different. Especially, the Rd of mineralized rock shows that almost no retention capacity expected. It might be due to the fact that the sorption sites are almost fully occupied probably by uranium[12].

The Rd of the unmineralized rock probably shows the similar

chemical retention capability which can be expected as original capacity in tuffaceous sandstone at the uranium embedded zone. However, the Rd of the unmineralized rock may regard as relatively smaller than in situ retention capability, because the in situ retardation factor includes not only chemical retention capability but also storage capacity of microscopic pore or path structure itself. Moreover, the in situ reducing condition will be more effective to increase chemical retention capability in the geological media, because of uranium(VI) reduction and precipitation as inferred from geochemical modelling of groundwater by PHREEQE code mentioned previously.

4 CONCLUSIONS

Geological and geochemical investigations of the uranium concentration zone were macroscopic and microscopically carried out in the Tono uranium deposit, and the followings are obtained.

(1)In the macroscopic scale, the governing factor of natural uranium concentration is not the geochemical retention capability but the permeable geometry which can provide the mass of natural uranium. The fact will suggest that the uranium contents shows the possible availability of total retension capacity of the host rock.

(2)In the microscopic scale, the uranium occurrence shows that the pore within the detrital grains played a major role of the nuclides transportation as the migration paths and/or the concentration fields.

Migration behaviour such as advection/diffusion and sorption in the pore or path seems to be strictly obeyed the void structures built up by constituent materials. The detail

characterization of pore and path structure, therefore, must be needed for development of a basic conceptual model of nuclides transport and comprehension of the retention mechanisms of sedimentary rock. Furthermore, such model development are required in order to qualitatively assess the migration process in geological media and improve the reliance of the performance assessment of far-field nuclides migration.

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Sampling point : -153m ~ -155m (mbgl)			
Temperature : 18.5℃			
Eh : -335mV			
pH : 9.2			
DO* : 0.0 ppb			
EC** : 168 μ S/cm			
Ion	Concentration(ppm)	Ion	Concentration(ppm)
Si	8.1	Na^{+}	45
Al	<0.02	K^{+}	0.29
Fe^{2+}	<0.02	F^{-}	4.1
Fe^{3+}	<0.02	Cl^{-}	1.06
Mn^{2+}	<0.01	SO_4^{2-}	1.26
Mg^{2+}	0.02	HCO_3^{-}	79
Ca^{2+}	1.98	CO_3^{2-}	8
U	0.15(ppb)		

DO* : Dissolved oxygen

EC**: Electric conductivity

Table 1. Characteristics of groundwater in the ore body zone.

Unmineralized Rock	Mineralized Rock
Quartz	Quartz
K-feldspar	K-feldspar
Albite	Albite
Biotite	Biotite
Calcite	Calcite
Hornblende	Hornblende*
Pyrite*	Pyrite
Smectite	-
Chlorite	Chlorite
U : 20ppm	U : 1.81%

Hornblende*, Pyrite* : very rare

Table 2. Major mineral compositions and uranium contents of rock samples of batch sorption study.

Tracer	U-233
Initial concentration	5.0 x 10E-7 M
Solution	Groundwater(See Table 1)
Volume	50ml
Specimen	Mineralized and Unmineralized rock
Grain size	$<710\ \mu$ m
Mass of specimen	19.6g
Temperature	20℃
Atmosphere condition	N_2
Analytical method	α -counting, α -spectrometry
Sampling time(days)	7, 14, 33, 60

Table 3. Experimental condition of batch sorption study.

		Rd(ml/g)	
Rock sample	Final pH	0.45um filtered	10,000MWCO filtered
M*	8.55	3.5±0.3	3.6±0.3
M	7.66	4.3±0.3	4.2±0.3
M	6.99	4.5±0.3	4.4±0.3
UM**	8.46	129.4±40	164.7±60
UM	8.70	92.8±30	58.8±10
UM	8.45	89.6±30	99.6±30

M* : Mineralized rock UM** : Unmineralized rock

Experimental duration = 60 days

Table 4. U-233 batch sorption results.

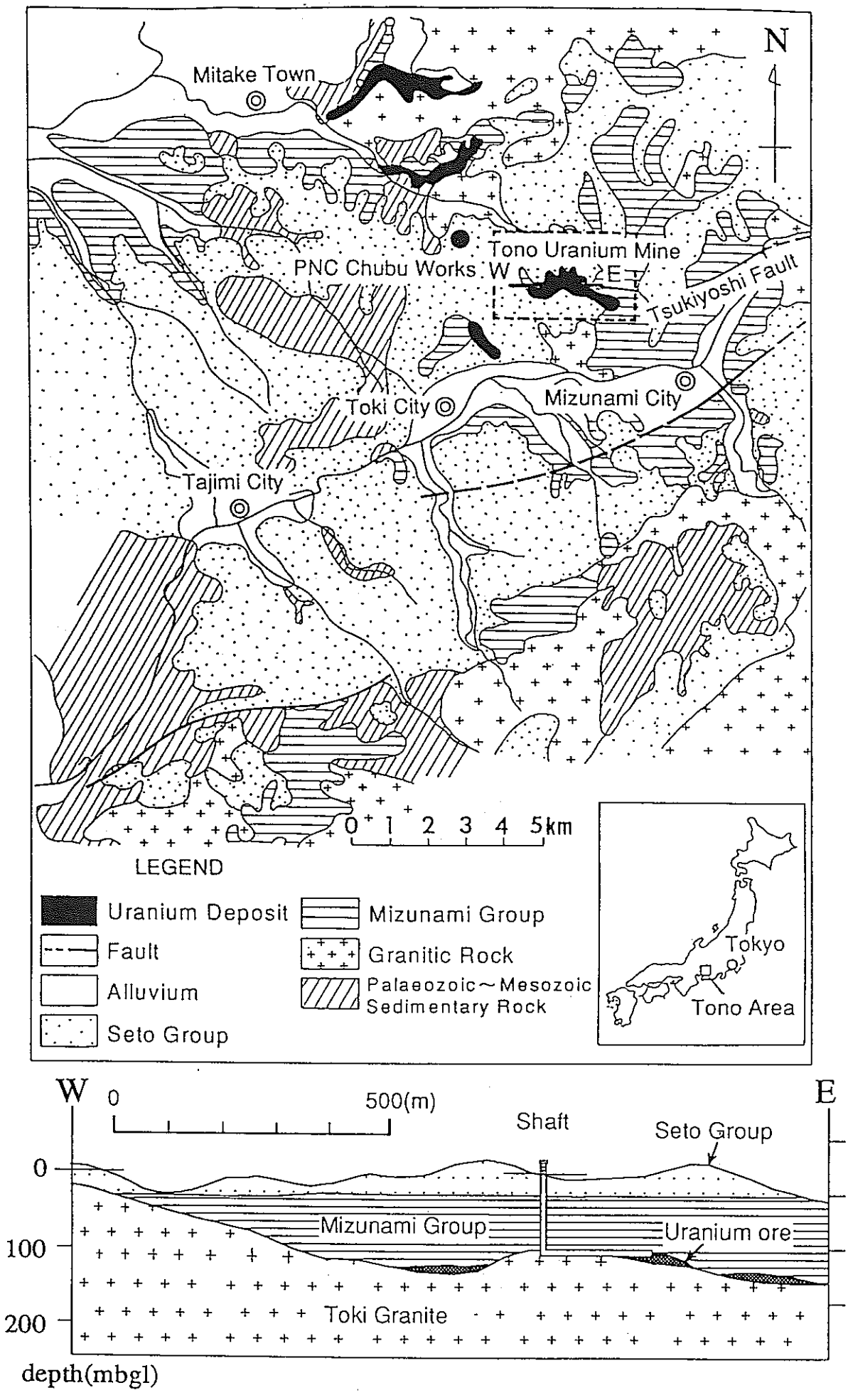


Figure 1. Geological map and cross section of the Tono uranium deposit.

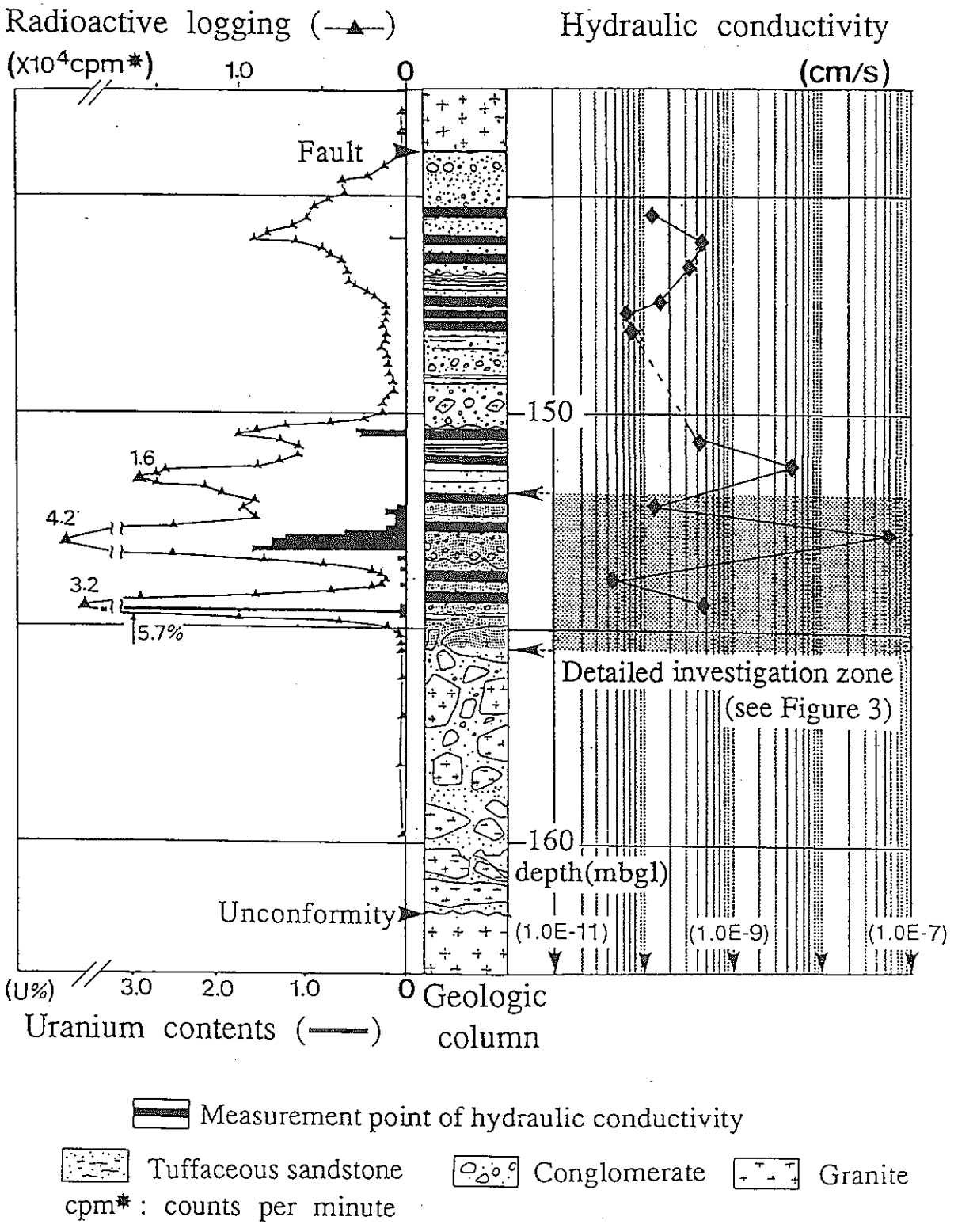
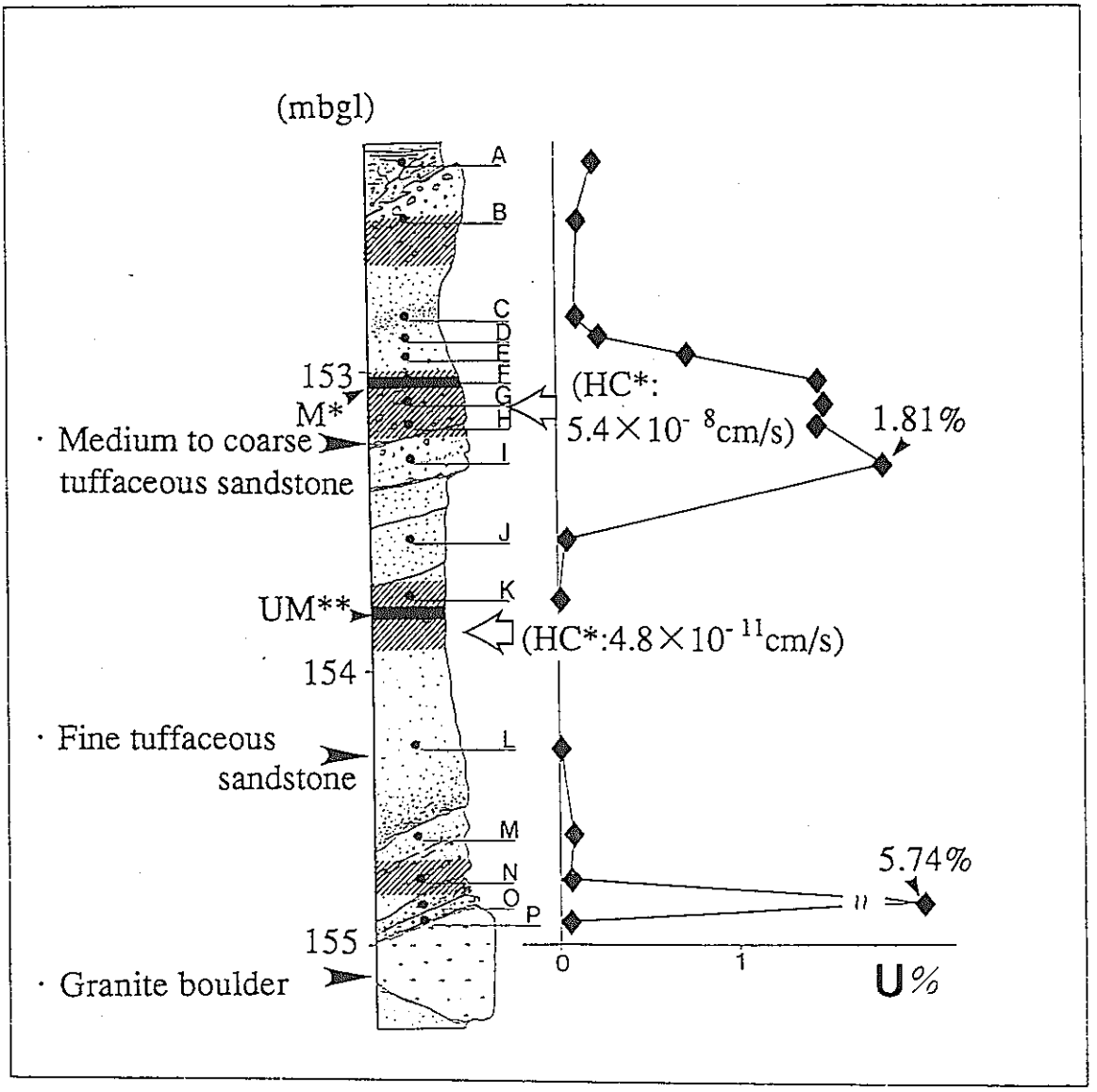


Figure 2. Radioactive logging and hydraulic conductivity measurements for the uranium embedded zone.



Measurement point of hydraulic conductivity.

Sampling point for U-233 batch sorption experiment.

(M*:Mineralized rock sample, UM**:Unmineralized rock sample)

A~P: Sampling point for microscopic observation and chemical analysis.

HC*:Hydraulic conductivity

Figure 3. Geological background of the rock, and groundwater sampling point for batch sorption experiment.

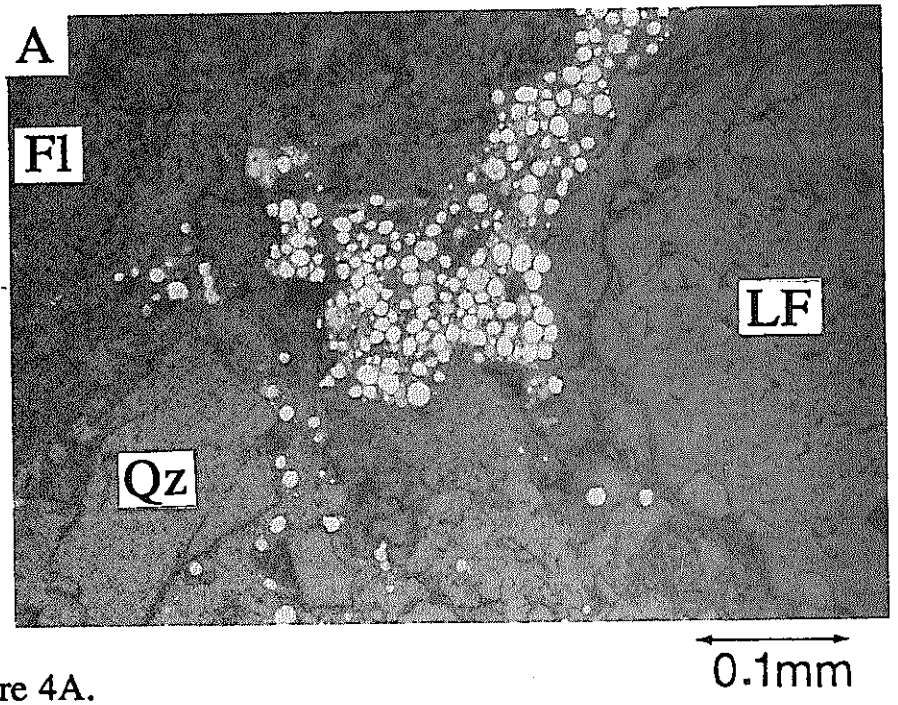


Figure 4A.
Photomicrograph(reflected light) showing framboidal pyrite(Py) precipitating among detrital grains (Fl:Feldspar, Qz:Quartz, LF:Lithic Fragment)

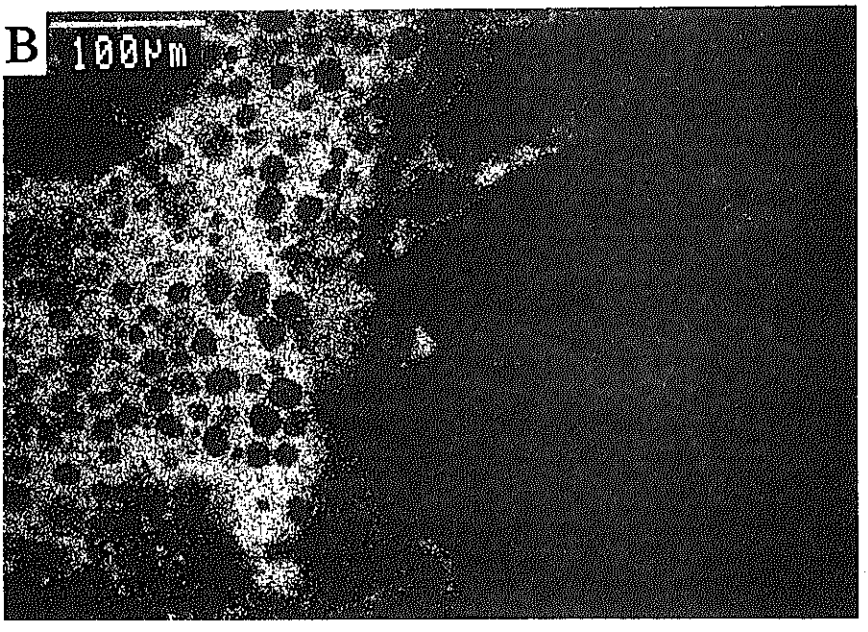
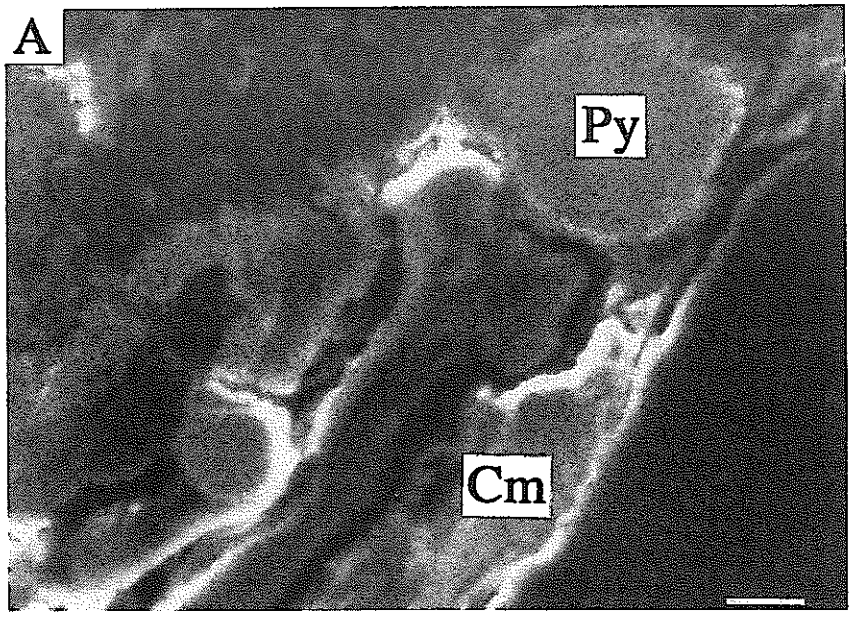


Figure 4B.
Characteristic x-ray photograph showing high concentration of natural uranium around the framboidal pyrite between detrital grains.



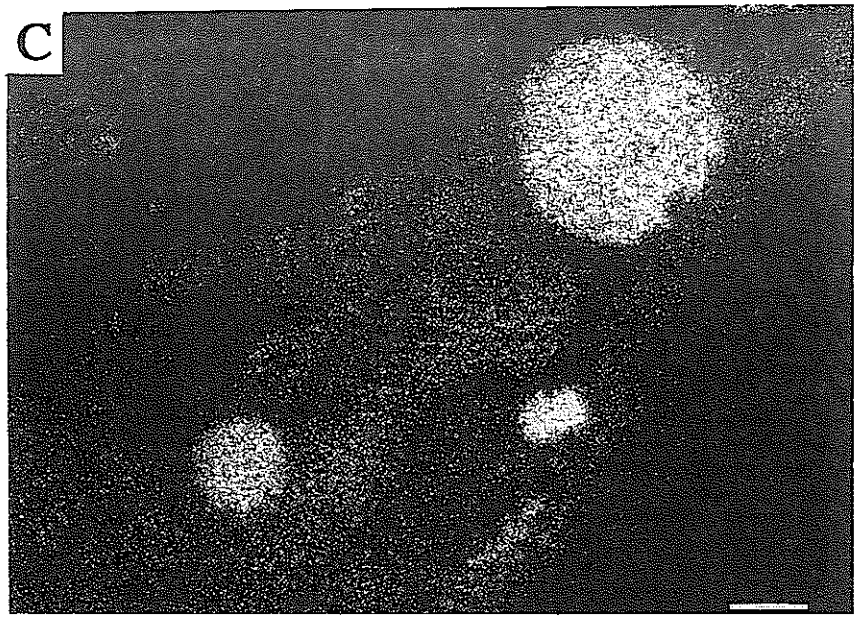


Figure 5.

SEM micrograph(A) and characteristic x-ray photographs (B: distribution of uranium, C:distribution of iron) showing close correlation between uranium, framboidal pyrite(Py) and clay mineral(Cm). (scale bar = 10 μ m)

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