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GEOCHEMICAL CHARACTERISTICS AND GENESIS OF SANDSTONE-TYPE URANIUM DEPOSITS, SIERRA PINTADA DISTRICT, SAN RAFAEL, MENDOZA, ARGENTINA

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ABSTRACT

The genesis of sandstone-type uranium deposits in the Cochicó Group (Permian, Permian-Triassic) at Sierra Pintada, the most important uranium district in Argentina, has been studied.

The uranium source and its transport and precipitation processes are discussed, as well as the geochemical characteristics of the environment, where uraninite and brannerite, the main uranium minerals, are associated to the matrix of the sandstone.

Several phenomena may be pointed out in the depositional environment: where oxygen is available, precipitation of the hydrated ferric oxides occurs; the CO_2 partial pressure in the environment determines whether α-or γ-Fe_2O_3 varieties are formed. Consequently, at upper aquifer levels or its rims, the γ-variety (identified by Mössbauer effect) prevails; it gives red, reddish-brown and red-violet colouring to the sandstone.

The partial pressure of CO_2 also determines the distribution of the uranium reducing agents. Thus a selective biogenetic action can be explained which is important at aquifer upper levels or its rims, where bacteria find the most favourable environment for their development. Consequently the highest concentrations of uranium minerals, precipitated at those levels with red, reddish-brown or red-violet colouring are produced there. It is thus possible to explain the association between high uranium contents and γ-ferric oxides observed in certain horizons within the host sandstone.

RÉSUMÉ

On étudie la genèse des dépôts uranifères dans les grès du Groupe Cochicó (Permien, Permien-Trias) à Sierra Pintada, le district uranifère le plus important de la Republique Argentine.

On discute la source de l'uranium, les processus de transport et de précipitation de cet élément ainsi que les caractéristiques géochimiques de l'environnement où se déposent l'uraninite et la brannerite, ceux qui sont les principaux minéraux de l'uranium qui s'y trouvent associés à la matrice de la roche-hôte.

On signale des différents phénomènes dans l'environnement où ces minéraux se déposent: là où il existe de l'oxygène disponible il se produit une précipitation des oxydes ferriques hydratés; la pression partielle de CO_2 dans l'environnement est le facteur determinant pour que les variétés α et γ de l'oxyde ferrique puissent se former. C'est ainsi qu'aux niveaux supérieurs et sur les bords de l'acuifère libre-là où la pression partielle de CO_2 est la plus basse- les variétés γ prédominent (elles sont identifiées au moyen de l'éspectroscopie Mössbauer). Ces variétés teintent le grès en rouge, châtain rougeâtre et rouge violacé.

La pression partielle de CO_2 détermine également la distribution des agents qui réduisent l'uranium. C'est ainsi que l'on peut expliquer une action biogénétique sélective qui n'a de l'importance qu'aux niveaux supérieurs de l'acuifère ou sur ses bords. Dans ces endroits les bactéries trouvent un milieu plus favorable pour leur développement. Par conséquence à ces niveaux teintés en rouge, châtain rougeâtre et rouge violacé c'est là où se produisent les plus importantes concentrations de minéraux d'uranium précipités. De cette façon il est possible d'expliquer l'association que l'on observe dans certain niveaux de grès porteur, entre haute concentration d'uranium et les oxydes ferriques de la variété γ.

INTRODUCTION

The Sierra Pintada, located between 69° - 65°W and 33° - 39°S, is a 3500 km^2 area geomorphological unit, a hilly strip with relatively smooth relief features, extending in NNW-SSE direction which appears limited on the west by a depressed zone separating it from the Cordillera Principal and, on the east, by an extended plain which is part of the geomorphological unit called "external depression of Mendoza"(González Díaz, 1964).

The Sierra Pintada uranium district (see Fig. 1) is located in the Province of Mendoza, 35 km west of the town of San Rafael. It consists of uranium deposits "Dr. Baulíes" (Tigre I and II sectors), "Los Reyunos" (La Terraza sector), "Tigre III", "Media Luna I and II", "Gaucho I and II" and many anomalies in a 400 km^2 area.

Up to the present it is the principal uranium district in Argentina. Its reserves are of the order of 16,000,000 tons of ore mineral of grades varying from 0.70 to 1.18‰ U_3O_8.

GENERAL GEOLOGY

The geology of the area has been studied by Polanski (1964), González Díaz (1964 and 1972), Rodríguez and Valdiviezo (1970), Ortega Furlotti et al., (1972), Criado Roque (1972), Criado Roque and Ibáñez (1979) and Pérez (1979). For various practical reasons the stratigraphic sequence (Fig. 2) established for the area by the Comisión Nacional de Energía Atómica (CNEA) has been adopted.

Small outcrops of Precambrian rocks (amphibolites, micacites, hornblendic schists, etc). and very small limestone outcrops, Cambrian - Ordovician age, unconformably overlying the Precambrian metamorphic rocks, occur in the geomorphological unit, but outside the area of the Sierra Pintada uranium district.

In the area of the uranium ore deposits and anomalies, the stratigraphic sequence is as follows:

Devonian. Wide outcrops belonging to La Horqueta Formation composed of greywackes, quartzites, mica schists, mica quartz schists, sericitic argillites and chlorite and sericite schists, corresponding to typical flysh deposits, which show variable degrees of metamorphism decreasing from north to south in the block. Plutonic rocks (grabbros, diorites and granodiorites intrude into those metamorphites.

Carboniferous. a) El Imperial Formation (Lower Carboniferous). Extended outcrops of silstones, green and carbonaceous shale and bituminous rocks characterizing a sea coast environment, gradually turning towards the upper part to quartzitic sandstones, conglomeradic reddish sandstones and conglomerates which are indicative of a transition to a depositional environment of a continental type.

b) Cerro Colorado Formation (Upper Carboniferous). Reddish and greenish conglomerates and breccias. This depositional cycle culminates in an orogenesis which gave origin to the strong angular unconformity between Carboniferous and Permian sediments.

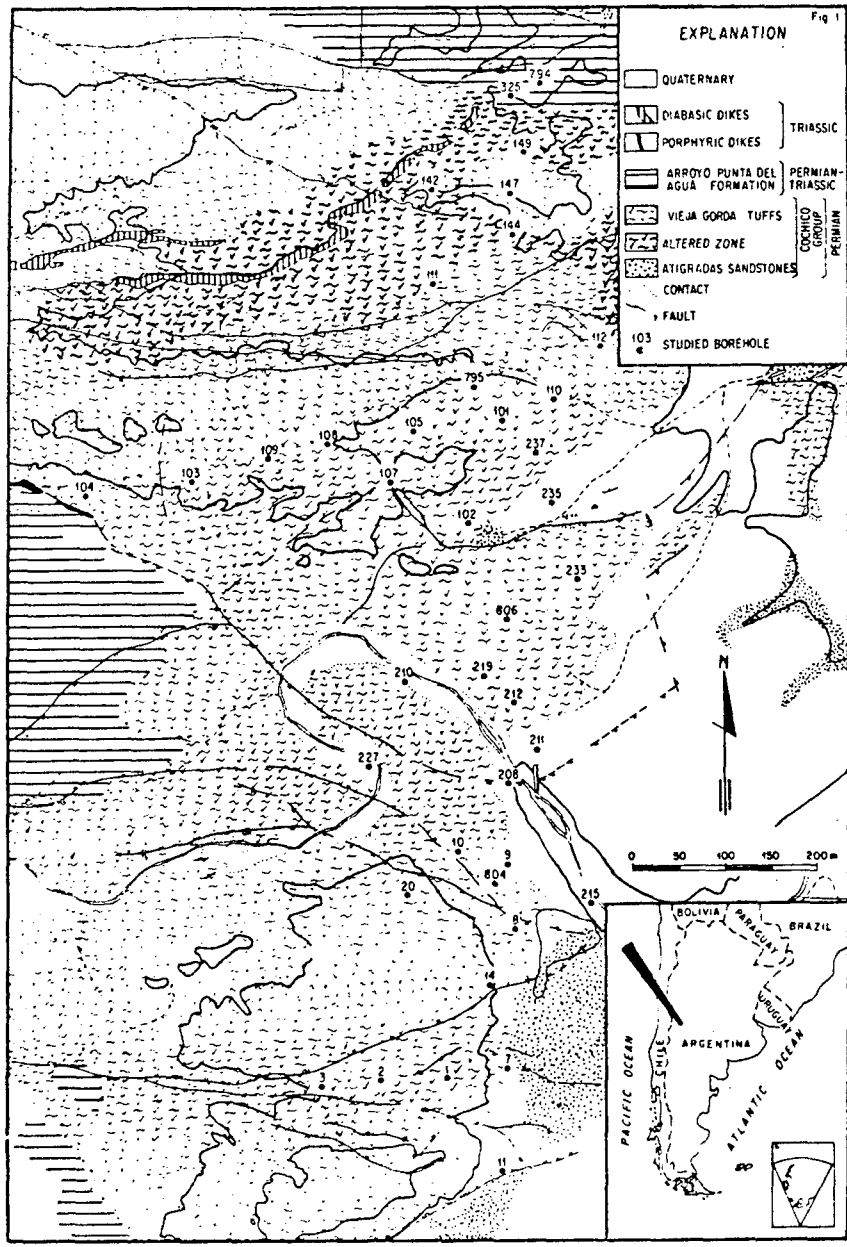
Fig 1
EXPLANATION
QUATERNARY
DIABASIC DIKES
PORPHYRIC DIKES
TRIASSIC
ARROYO PUNTA DEL AGUA FORMATION
PERMIAN-TRIASSIC
VIEJA GORDA TUFFS
ALTERED ZONE
ATIGRADAS SANDSTONES
COCHICO GROUP
PERMIAN
CONTACT
FAULT
103 STUDIED BOREHOLE
N
0 50 100 150 200 m
BOLIVIA
PARAGUAY
BRAZIL
URUGUAY
CHILE
ARGENTINA
PACIFIC OCEAN
ATLANTIC OCEAN

Permian. Cochicó Group. Detritic sediments with intercalated pyroclasts. It comprises two formations:

a) Yacimiento Los Reyunos Formation. Composed of three members:

   i) Psephitic Member. Polymictic ortho-conglomerates ("red conglomerate") and fanglomerates with sandstone intercalations and two pyroclastic levels; the lower one is conglomeradic and the higher one is tuffaceous.

   ii) Atigradas Sandstones Member. Fine to coarse grained arkoses (see Appendix) with parrallel and cross-bedded stratification. Intercalation of tuffaceous levels.

   iii) Vieja Gorda Tuff Member. Crystallolithic tuffs mainly of rhyodacitic composition and porphyroclastic texture. Some conglomeratic levels are present.

b) Arroyo Punta del Agua Formation. (Permian-Triassic?). Reddish sandstones and conglomerates with pyroclastic and tuffaceous material increasing in the upper levels.

Permian - Triassic. Cerro Carrizalito Group. It comprises the following formations:

a) Quebrada del Pimiento Formation. Basaltic facies.

b) Agua de los Noques Formation. Dacitic facies.

c) Cerro Carrizalito Formation. Rhyodacitic-rhyolitic facies.

Triassic. Puesto Viejo Formation. Massive succession of continental sediments from coarse conglomerates to ignimbritic tuffs. Intercalated basic to andesitic sills and dykes.

Tertiary. The Miocene epoch marks the reinitiation of the depositional cycle after peneplanation. It comprises two formations:

a) Aisol Formation (Miocene). Continental sediments mainly sandstones and silty sandstones.

b) Río Seco del Zapallo Formation (Pliocene). Continental sediments mainly fine grained sandstones with pyroclastic material, conglomeradic limestone and sandy limestone intercalations.

There occur intercalated basaltic and andesitic sheets.

Quaternary. Continental sediments: alluvial, aeolian and piedmont sediments, etc. Basaltic and andesitic flows and pyroclastic levels. Calcareous rocks of hydrothermal origin.

The tectonic activity in the area starts in the Precambrian with predominant E-W fractures, but starting with the Precambrian-Paleozoic boundary the zone exhibits a predominantly N-S fracturing which defines the main structural features. The processes of the Acadic Bretonic Movements affected the sedimentary phase of La Horqueta Formation which presents a compressive tectonic with thrusts from the western sector. El Imperial Formation undergoes the initial phase of the Variscic

SIERRA PINTADA URANIUM DISTRICT
SIMPLIFIED STRATIGRAPHIC SEQUENCE

ERA-THEM	SYSTEM	SUBSYSTEM	SERIES	GROUP	FORMATIONS and Members	LITHOLOGY and FACIES	AGE DETERMINATIONS (m.y.) (Toubes and Spikermann 1976 and 1979)
CENOZOIC	QUATERNARY		HOLOCENE PLEISTOCENE		SEVERAL FORMATIONS	Alluvial, aeolian and piedmond sediments, etc Basaltic and andesitic flows.	Basalt 1,5 ± 1
	TERTIARY	NEOGENE	PLIOCENE		RIO SECO DEL ZAPALLO	Mainly fine grained sandstones; intercalated basaltic and andesitic sheets	Basalt 3,2 ± 1
			MIOCENE		AISOL	Mainly sandstones	Basalt 13 ± 0
						PENEPLANATION	
MESOZOIC	TRIASSIC		UPPER MIDDLE LOWER		PUESTO VIEJO	Massive succession of continental sediments	Granodiorite porphyry 192 ± 6
						DISCONFORMITY	
	PERMIAN-TRIASSIC			CERRO CARRIZALITO GROUP	CERRO CARRIZALITO	Rhyodacitic - rhyolitic facies	Rhyolite porphyry 219 ± 15 Rhydacite porphyry 223 ± 10 Granite porphyry 238 ± 10 Rhyolite 241/244 ± 10 Granophyre 247 ± 10
					AGUA DE LOS NOQUES	Dacitic facies	
					QUEBRADA DEL PIMIENTO	Basaltic facies	Basalt porphyry 259/260 ± 10 Granophyre 262 ± 10
	?					UNCONFORMITY	
				COCHICO GROUP	ARROYO PUNTA DEL AGUA	Mainly reddish sandstones and conglomerates	
						UNCONFORMITY	
PALEOZOIC	PERMIAN		LOWER		YACIMIENTO LOS REYUNOS — Vieja Gordo Tuff Member	Mainly crystallolithic tuffs	Crystallolithic tuff 272 ± 10
					Aligrados Sandstones Member	Fine to coorse - grained arkoses	
					Psephitic Member	Mainly conglomerates and fanglomerates	
						UNCONFORMITY	
	CARBONIFEROUS		UPPER		CERRO COLORADO	Mainly conglomerates	Andesite 281 ± 10 Microtonalite 285 ± 10
			LOWER		EL IMPERIAL	Seacoast and continental sediments	
	DEVONIAN				LA HORQUETA	Mainly marine sediments	Schist 353 ± 15

Movements which is the strongest of the subsequent phases. These last throughout the Permian, affecting the pyroclastic facies, indicative of a strong contemporary volcanism. The orogenic activity of the Asturic phase closes the Carboniferous cycle and the sedimentation of the Cochicó Group starts; it occurs in an unstable zone with basement movements and contemporary magmatic activity which occur as great tuffaceous contributions and injections of porphyry and other varied-composition rocks. From then on, the tectonic activity follows a classical taphrogenic style (Criado Roque and Ibáñez, op. cit.). These fractures must have played a significant role in the Permian-Triassic effusions.

The interpermic movements gave rise to a new magmatic cycle, represented by rocks of the Carrizalito Group with facies showing progressive acidification. There follows a quiet period until the Middle Triassic where continental sedimentation prevails with scarce volcanic activity, indicative of the smooth accompanying tectonism.

During the Mesozoic, the area is uplifted and, consequently, subjected to erosive processes. Some sediments corresponding to the Tertiary superposed to the Sierra Pintada Complexes can only be distinguished; they are outcrops showing very little structural deformation due to the regidity acquired by the basement (bedrock) on which they lie. During the Tertiary, the different phases of the Andean cycle operated in the zone, but their action was of a taphrogenic nature with implantation of multiple fractures.

The later ascent of Sierra Pintada was accompanied by basaltic flows during the neotectonic phase in the lower Pleistocene.this was followed by the beginning of the formation of the San Rafael plain, with the contributions of successive alluvial levels which gave rise to the present morphological features (Pérez, op. cit.).

SAMPLING AND LABORATORY STUDIES

In the Sierra Pintada uranium district many costeanings and trenchings were sampled and, in strategically selected places, geological profiles and systematic samplings of lithological units were made, over 270 samples being collected.

From the 380 drillings, 50 were selected for laboratory analysis. The systematic mineralogical studies comprised over 50 samples; more than 350 thin sections and 40 polished sections were examined. The granulometric analysis and the sedimentological study comprised more than 130 samples.Over 400 samples were selected for chemical analysis and 10 samples for studies by Mössbauer spectroscopy.

MINERALOGY

The mineralogical determinations carried out by E. Arcidiacono and M.E. Saulnier (1979) comprised macroscopic studies, heavy liquid separations, detailed studies of polished sections complemented by microchemical tests, X-ray diffraction, X-ray flourescence and electron microprobe analysis.

Said studies led to the determination of an interesting mineral association where uranium minerals (uraninite, brannerite, uranophane and coffinite) were found as well as sulfides (mainly pyrite and lesser amounts of arsenopyrite, chalcopyrite, bornite and marcasite). These minerals were accompanied by clastic rutile, titanomagnetite, zircon, barite and apatite, and also by anatase, siderite, dolomite, cal-

cite, hematite, other ferric oxides and clay minerals (montmorillonite, illite and kaolinite). Organic matter was present associated to uranium minerals.

The main characteristics of some uranium minerals and anatase are described below for a better understanding of the genesis of ore deposits:

Uraninite

This is probably the most abundant uranium mineral in the deposit under survey. The term uraninite is used with reference to its morphology, since it occurs in well developed subhedral to tabular crystalline forms, skeleton or vein-like shapes. However, this uraninite presents low thorium and cerium contents and a high calcium content, which are common features of UO_2, precipitated as pitchblende (colloform variety). The average size of the tabular crystals is 150 microns. Uraninite usually occurs in the sandstone matrix, where it may surround clasts or traverse them as filling and replacement veinlets (see Plate I;4).

Brannerite

It occurs frequently associated to anatase and organic matter. Its optical properties ressemble those of uraninite. It appears in tabular forms with common round aggregates of up to 250 microns (the average size of the aggregates is about 35 microns).

The variability in its hazel grey internal reflexions and reflectivity is associated with little compositional changes in association with anatase.

In this connexion it is interesting to remark the different degrees of replacement of anatase by brannerite. Said replacement can be considered centrifugal (Edwards, 1954): subrounded anatase with incipient brannerite core until complete replacement producing a pseudomorphosis of brannerite after anatase (Plate I; 1, 2, 3).

This has been proved by electron microprobe analysis on a rounded brannerite crystal. On the rims of this crystal a greater concentration of titanium without uranium was found in coincidence with the optical observations of brannerite exhibiting a sligth rim of anatase (Plate I; 5, 6). These images prove the introduction of uranium after the formation of anatase: the image corresponding to titanium distribution shows microfractures wich are no longer visible in the image corresponding to uranium distribution.

In some cases the replacement is centripetal.

Anatase

It is a common mineral in the samples of Atigradas Sandstones Member. It usually occurs as subrounded polycrystalline aggregates or as small single subhedral crystals of a size close to 150 microns. Optically the internal reflexions show colour variations, which would be explained by the presence of uranium. And in fact the presence of uranium was corroborated by electron microprobe thus proving an incipient centripetal replacement.

TABLE I

CHEMICAL ANALYSIS METHODS

Constituent	Method	References
U<120 ppm	Fluorimetry after chromatographic separation.	BERTHOLLET, 1968
U>100 ppm	Spectrophotometry of U-DBM complex.	YOE et al., 1953; D'ALESIO and CAPACCIOLI, 1962
FeO	Dichromate titration.	SHAPIRO, 1975
Fe_2O_3 (total iron)	Dichromate titration.	PECK, 1964
TiO_2	Spectrophotometry of peroxidized solution.	PECK, 1964; GRILLOT et al., 1964.
MnO	Spectrophotometry of permanganate.	SHAPIRO, 1975
P_2O_5	Spectrophotometry of molybdovanadophosphoric acid complex.	SHAPIRO, 1975
$SO_4^{=}$	Turbidimetry of barium sulphate.	SHAPIRO, 1975
Se	Spectrophotometry of 3,3'-diaminobenzidine complex.	BARCZA and SOMMER, 1962
Mo	Spectrophotometry of Mo-thiocyanate complex.	WARD et al., 1963.

TABLE II

STATISTICAL ANALYSES

Element distribution in sandstones

Hypothesis: lognormal distribution

Surface samples

	n	Range		$\bar{x}$	qm	s^2	sk	k	$P(\chi^2)$
		from	to						
U ppm	41	0.3	9.2	1.55	1.06	3.02	2.3	6.90	0.93
FeO %	42	0.14	1.00	0.35	0.33	0.03	1.39	4.75	0.95
Fe_2O_3 %	43	0.11	4.38	1.72	1.40	0.86	0.37	2.82	0.93
Fe_2O_3 % (Total Fe)	42	0.39	4.20	2.05	1.89	0.71	0.34	2.74	0.92
TiO_2 %	43	0.12	0.69	0.35	0.33	0.015	0.44	3.05	0.92
P_2O_5 %	43	0.012	0.20	0.09	0.07	0.002	0.73	3.34	0.92
MnO %	42	0.004	0.08	0.034	0.028	0.0007	1.53	5.77	0.91
$SO_4^=$ %	21	0.66	1.80	0.80	0.76	0.10	2.73	8.53	*
Se ppm	20	0.14	2.7	0.99	0.73	0.53	0.88	2.87	*
Mo ppm	36	2.1	22.2	9.76	8.70	25.04	0.67	3.04	0.93
* not enough data available									
Drill core samples									
U (< 40 ppm)	105	0.85	40.	9.16	6.12	80.81	1.31	3.54	0.85
U (> 40 ppm)	110	40.	6106.	661.	-	935806	2.49	10.61	0.84
FeO %	115	0.04	2.13	1.05	0.91	0.25	0.35	2.55	0.84
Fe_2O_3 % (Total Fe)	101	0.97	4.75	2.58	2.50	0.47	0.77	3.66	0.86
TiO_2 %	52	0.15	0.65	0.36	0.35	0.011	1.10	4.65	0.91
P_2O_5 %	96	0.002	0.16	0.09	0.09	0.0014	-0.04	3.57	0.85
MnO %	57	0.005	0.99	0.08	0.04	0.024	0.67	3.57	0.90
Se ppm	39	0.1	10.5	1.78	1.22	2.73	1.93	6.07	0.92
Mo ppm	61	1.65	26.6	12.11	11.07	21.84	0.68	3.44	0.89
Hypothesis: normal distribution									
Drill core samples									
Fe_2O_3 %	99	0.29	4.11	1.34	1.13	0.73	1.03	3.59	0.84
$SO_4^=$ %	33	0.66	0.90	0.72	0.72	0.0024	1.57	6.07	0.92

TABLE III

Correlation coefficients between pairs of elements in sandstones

Surface samples

	U	FeO	Fe_2O_3	Fe_2O_3 Total Fe	TiO_2	P_2O_5	MnO	$SO_4^=$	Se	Mo
U	-									
FeO	0.303	-								
Fe_2O_3	-0.123	-0.106	-							
Fe_2O_3 (Total Fe)	-0.044	0.121	0.990	-						
TiO_2	0.164	0.183	0.204	0.308	-					
P_2O_5	0.262	0.154	0.216	0.316	0.566	-				
MnO	-0.052	0.192	-0.041	0.151	0.112	0.195	-			
$SO_4^=$	0.067	-0.038	0.452	-0.017	-0.307	-0.045	0.294	-		
Se	0.397	-0.161	-0.058	0.042	0.143	0.361	0.274	-0.009	-	
Mo	-0.031	0.062	0.203	0.216	-0.080	-0.196	0.031	0.007	0.396	-
N	41	42	43	42	43	43	42	21	20	36

Drill core samples

	U	FeO	Fe_2O_3	Fe_2O_3 Total Fe	TiO_2	P_2O_5	MnO	$SO_4^=$	Se	Mo
U	-									
FeO	-0.083	-								
Fe_2O_3	-0.071	-0.096	-							
Fe_2O_3 (Total Fe)	0.124	0.054	0.734	-						
TiO_2	0.030	0.180	-0.067	0.378	-					
P_2O_5	0.096	-0.028	0.066	0.043	0.520	-				
MnO	-0.014	0.034	0.058	0.026	-0.019	-0.001	-			
$SO_4^=$	-0.155	0.098	-0.220	0.026	-0.157	-0.176	0.002	-		
Se	-0.139	-0.041	-0.016	-0.050	0.032	-0.193	-0.188	-0.233	-	
Mo	0.048	0.097	0.138	0.067	-0.062	-0.205	-0.092	0.188	0.200	-
N	215	115	99	101	52	96	57	35	39	61

Coffinite

It occurs in crystalline aggregates. It is associated to uraninite, pyrite and organic matter (Plate I, 4) and usually cements the clasts of the host rock. Of a dark grey colour, it compares with uraninite or brannerite. It is faintly anisotropic and does not present internal reflexions.

CHEMICAL ANALYSES

Four hundred and fourteen samples were analysed; 258 of them corresponded to the Atigradas Sandstones Member (43 surface samples and 215 drill core samples) and 156 corresponded to the Vieja Gorda Tuff Member (56 surface and 100 drill core samples). The analytical methods used are listed in Table I.

STATISTICAL ANALYSIS

Table II shows the results* of statistical distribution analysis of the elements in sandstones, supposing a lognormal or normal distribution. The listing includes: n (number of analysed samples), $\bar{x}$ (weighted arithmetic mean), gm (geometric mean), s^2 (sample variance), sk (skewness), k (kurtosis), $P(\chi^2)$ (probability cumulative distribution function at a 95% confidence level). When $P(\chi^2)$ is not greater than 0.95, the distribution hypothesis is confirmed.

All cases show a good fit to the lognormal distribution, except Fe_2O_3 and $SO_4^=$ in the drill core samples which fit the normal distribution.

Table III presents the results** corresponding to the correlation coefficients (r). Since the r values are very low, it is concluded that there is no correlation between uranium and the chemical elements considered.

MÖSSBAUER SPECTROSCOPY

Ten samples of sandstones were analysed by Mössbauer spectroscopy. The Mössbauer spectra were measured in a transmission geometry with an Elron Mössbauer spectrometer in a constant acceleration mode with an Ar/CO_2 filled Reuter Stokes R.S.G.-61-M2 proportional counter. Spectra were displayed in a multichannel analyzer operated in the time mode. The source used was ^{57}CO in Pd matrix, and the samples, in powder form, were weighed out to give an iron constant of approximately 10 mg/cm^2 and were encapsulated between thin acrylic disks. Measurements were carried out with the source at room temperature and the absorbers at room and liquid nitrogen temperatures. Spectra were least-squares fitted (Bunbury, 1974) employing a pure Lorentzian shape and constraining the corresponding peaks. The quality of the computer fit was checked by a χ^2-test and only those of lower value were accepted. The Mössbauer spectra of three samples are shown in Fig. 3, 4 and 5. Their parameters at room temperature are shown in Table IV.

*Programmes and subroutines of the TI.59, Texas Instrument Computer, for analysis of variance data, histogram data, means and moments, histogram construction and χ^2 distribution.

**TI.59 programme for linear regression.

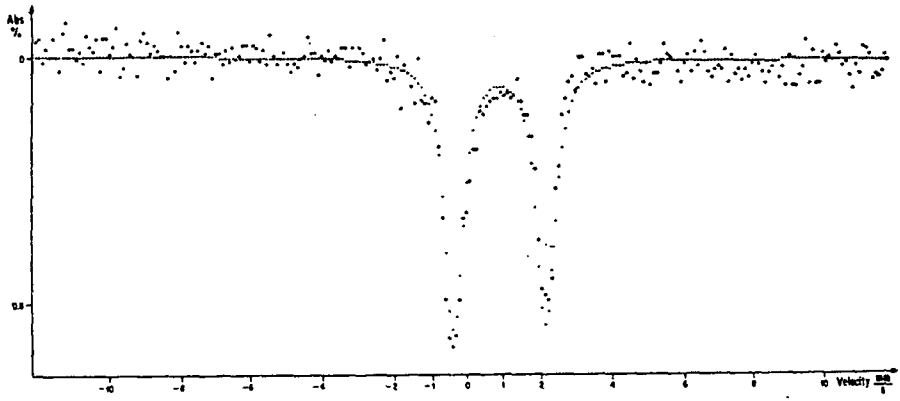

Fig. 3: Mössbauer spectrum of sample No. 39022 at room temperat.

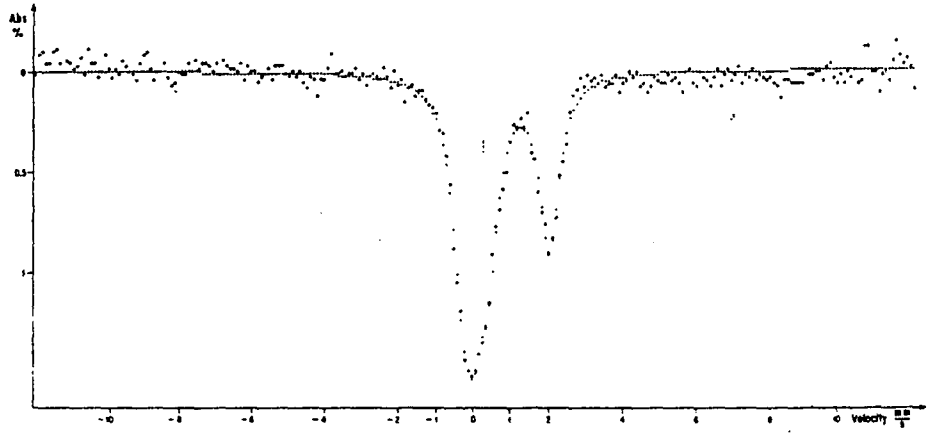

Fig. 4: Mössbauer spectrum of sample No. 39074 at room temperat.

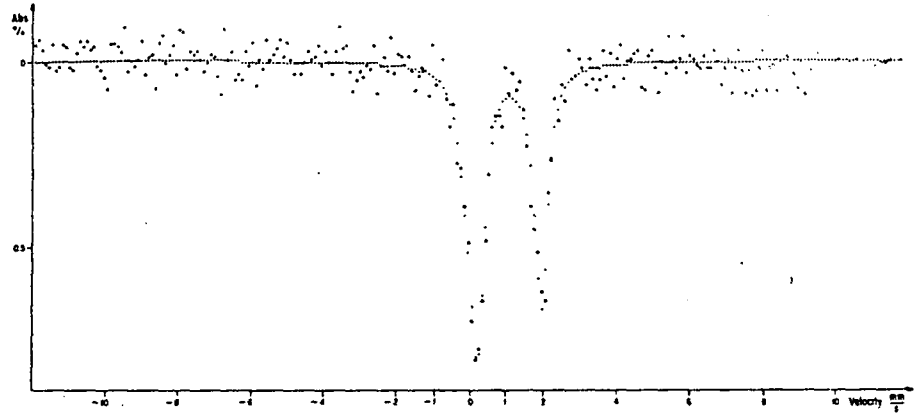

Fig. 5: Mössbauer spectrum of sample No. 737/78 at room temp.

The Mössbauer parameters of sample No.39022 indicate the presence of Fe^{+2} ion belonging to a mineral of the chlorite series. The QS values at room and liquid-nitrogen temperatures point out a distortion in the Fe^{+2} octahedron (Bancroft et al., 1967; Malysheva et al., 1977).

The parameters of sample No.39074 show the presence of Fe^{+2} and Fe^{+3}. The Fe^{+2} ion belongs to a mineral of the chlorite series and the QS values indicate a greater distortion of the Fe^{+2} octahedron than in the former sample. This Fe^{+2} represents 57% of the total iron content. The second doublet, Fe^{+3}, could be assigned to γ-$Fe_2O_3.H_2O$ (Dezsi et al., 1969) or to the chlorite or both. The Fe^{+3} in the chlorite could be adscribed to oxidation probably caused by decomposition of the crystal OH group.

From the Mössbauer spectra of sample No.737/78, it can be concluded that the main component is the Fe^{+2} of the chlorite in sites more distorted than in the samples mentioned above. This Fe^{+2} represents 84% of the total iron content; the other component is Fe^{+3} and in this case the corresponding parameters indicate the presence of γ-$Fe_2O_3.H_2O$ but the Fe^{+3} possible contribution from the chlorite cannot be completely discarded.

TABLE IV

MÖSSBAUER PARAMETERS AT ROOM TEMPERATURE

Sample	IS* mm/s	QS mm/s	IS* mm/s	QS mm/s
ee.39022	0.98 ± 0.02	2.58 ± 0.03		
ee.39074	1.04 ± 0.02	2.07 ± 0.03	0.08 ± 0.03	0.70 ± 0.02
737/78*	1.06 ± 0.02	1.78 ± 0.03	0.11 ± 0.03	0.50 ± 0.02

* referred to Pd matrix at room temperature

PIGMENTATION OF SANDSTONES

In all field studies performed on the host rock it has been noticed that the higher uranium concentrations correspond to reddish-brown or red-violet coloured beds. For that reason the aim has been to establish the differences in U_3O_8 content and the identification of the accompanying pigments through the mineralogical and chemical study of surface and drill core samples.

In general, red or reddish -brown coloured sandstones on the one hand and ochre coloured on the other, correspond to certain oxides or hydrated oxides of iron (Fe^{+3}) with different degrees of hydration. Those oxides were deposited with the matrix of the sandstones, usually in the form of a patina on grains of quartz and feldspars, or on the other principal or secondary mineral constituents. Said oxides were precipitated from ground waters to form, even into the same aquifer, red and ochre pigmen. .

TABLE V

STUDIES BY MÖSSBAUER SPECTROSCOPY

SAMPLE No.	SAMPLING surface borehole	U_3O_8 %	RADIOMETRY c/s	COLOURING	MINERALS IDENTIFIED BY MÖSSBAUER EFFECT	REFERENCE
ee.34107	Surface (trenching)	n.d.	50	Grey, ochre	Chlorites	NICOLLI, 1972, pp. 237-238
219/94	Borehole No.219 (core sample 94.2 m deep)	n.d.	40	Grey, olive-grey	Chlorites	NICOLLI et al., 1973, pp. 159-161
ee.39022	Borehole No.110 (core sample 54 m deep)	0.0002	n.d.	Grey	Chlorites	Present paper (Fig.3)
ee.34106	Surface (trenching)	n.d.	1800	Red-violet	Chlorites, γ-Fe_2O_3 (maghemite)	NICOLLI, 1972, pp. 237-238
219/64	Borehole No.219 (core sample 63.9 m deep)	0.3	600	Reddish	Chlorites, γ-Fe_2O_3 (maghemite)	NICOLLI et al., 1973, pp. 159-161
ee.39074	Borehole No.110 (core sample 66 m deep)	0.2	n.d.	Light reddish-brown	Chlorites, γ-$Fe_2O_3.H_2O$ (lepidocrocite)	Present paper (Fig.4)
737/78	Borehole No.906 (core sample 353 m deep)	n.d.	480	Light reddish	Chlorites, γ-$Fe_2O_3.H_2O$ (lepidocrocite)	Present paper (Fig.5)

n.d.= non determined

Many experiments have been performed to determine the nature of the ferric oxides precipitating from iron salts, usually carbonates. Red pigments develop as a patina on the surface and ochre pigments precipitate into the solution. Likewise sand mixed with a solution of an iron salt, exposed to the air, gives a reddish synthetic sandstone on the surface and an ochre synthetic sandstone in the midst of the solution (Hofer and Weller, 1947). The study of the structure of those iron oxides by X-ray diffraction enables the identification of γ-$Fe_2O_3.H_2O$ lepidocrocite (reddish-brown pigment) and α-$Fe_2O_3.H_2O$, goethite (ochre pigment).

The reason for the γ-varieties of ferric oxide to appear on the surface and the α-varieties at deeper levels clearly arises from these two facts: in a HCO_3^- solution, the partial pressure of CO_2 is higher in the midst of the solution and it decreases to reach a minimum at the surface; on the other hand, a low CO_2 concentration favours the formation of γ-$Fe_2O_3.H_2O$ versus α-$Fe_2O_3.H_2O$. Similarly, the γ-varieties of ferric oxide occur at the surface and higher levels of an aquifer and the α-varieties in its lower levels.

However, lepidocrocite is unstable, turning into γ-Fe_2O_3, maghemite (red pigment). Maghemite is, in turn, metastable, slowly becoming α-Fe_2O_3, hematite (red pigment). It was assumed that reddish, reddish-brown or red-violet beds (high uranium contents) were due to partial decomposition or transformation of lepidocrocite into the above mentioned ferric oxides (Nicolli, 1972). Consequently, detailed mineralogical and chemical studies of iron oxides were performed. Pigments from sandstone surface and drill core samples were analysed by Mössbauer spectroscopy Nicolli, op. cit; Nicolli et al., 1973) at room temperature and at liquid-nitrogen temperature, using $^{57}Co/Cu$ and $^{57}Co/Pd$ sources. Table V shows some results of the studies performed at that time and of recent ones which contribute new data for the understanding of the problem.

GENESIS OF THE URANIUM DEPOSITS

For the analysis of the main problems related to the genesis of sandstone-type uranium deposits, at the Sierra Pintada district, three factors were considered: a) the uranium source; b) the element transport phenomena; and c) the process leading to uranium concentration and precipitation.

When reference is made of an uranium concentration source there appear different controversial hypotheses. The importance of granitic rocks as uranium source has always been pointed out, as well as the possibility of uranium introduction in the ground water cycle by means of hydrothermal fluids related to igneous acid rocks. However, there are no evidences at the Sierra Pintada district that may lead the authors to assume the action of ascendent hydrothermal solutions. The local structures study has revealed that the faults displace the uramium ore; this shows that they belong to a later age, probably contemporaneous to the Sierra Pintada block fracturing, which occurred in the late Tertiary.

Actually, the analysis of many tuff samples gives an uranium content lower than 2 ppm U. These are very low values for this type of rock and it means that the uranium leaching processes have been taking place as a result of the devitrification process observed in the original vitreous material. The logical assumption then is that the overlying or colateral tuffs, or those intercalated into the host rock, have been an important source of uranium. In the Sierra Pintada district there is also evidence of various acid volcanic processes of Permian-Triassic age

with outcrops of quartz porphyries whose radiometric values are much higher than those of the regional background and may also be considered as uranium sources. A genesis of uranium bearing rock by destruction of eruptive rocks is suggested by the presence of volcanic lithic clasts, well developed crystalline faces and perfect bipyramidal forms in clastic quartz (see Appendix Point 1). It has been shown that the clasts in the arkoses had been subjected to little transport in an environment of steep slopes. Grain size and feldspars composition and alternation could mean a nearby rhyodacitic source. Histograms and cumulative curves are similar to the ones drawn for dune sands (Krumbein, 1963; Pettijohn, 1963), in good agreement with field study results. The intensity of the eolic transporting agent has varied with time, hence the alternance of layers of fine, medium and coarse size grains.

Rounded quartz originates in rhyolite phenocrysts and the remaining angular clasts, in other volcanic rocks. There are minor amounts of clay material and a regular proportion of carbonates (2 to 10% $CaCO_3$), most of them totally or partially replacing plagioclase clasts (carbonatization process). The alteration of the volcanic glass in lithic clasts (devitrification processes) may have also contributed uranium which in a second stage was redistributed throughout the uranium bearing sandstone. That is why in certain sectors a local association has been observed between uranium minerals and montmorillonite, clay mineral resulting from the alteration of volcanic glass(Chaar and Latorre, 1970; Nicolli et al., 1973).

The leached uranium entered the cyele of groundwaters to be redistributed together with other elements (Ca, Fe, $CO_3^{=}$, etc). These uranium bearing solutions moved in the form of a free aquifer through the Atigradas sandstones. The high permeability of the rock due to the lack of consolidation (incipient diagenesis) helped this ground water circulation process. The underlying "red conglomerate" (under the Atigradas sandstones) with intercalated pelitic levels served as a base for the water table, thus facilitating the process. In this sense, it is interesting to observe that the distribution of red, reddish-brown and red-violet pigments corresponds to more or less horizontal beds which are parallel to the base of the water table. Said distribution does not depend on the spatial distribution of the sandstone clasts of various characteristics (size, shape, composition, and alteration type and intensity).

In that environment the mobility of uranium was facilitated by the formation of carbonate complex ions, mainly UDC, $[UO_2(CO_3)_2(H_2O)_2]^{-2}$ and UTC, $[UO_2(CO_3)_3]^{-4}$. Both are very stable, UDC prevailing at pH<6.5 and UTC prevailing at pH>6.5; they can give rise to the migration of important amounts of uranium. The stability of the UDC and UTC complexes depends on the physico-chemical conditions of the environment, mainly on pH, Eh and CO_2 partial pressure in uranium bearing solutions. Any important change in the values of these parameters could produce the decomposition of the complex ions and the subsequent precipitacion of UO_2.

If the phenomena related to sandstone pigmentation, the petrographic features of the host rock and the mineral paragenesis observed in the uranium ore bodies are taken into account, local low temperature reduction processes may be inferred. In order to establish the nature of these processes it must be considered that the variations in the values of the redox potential (Eh) determined by the liberation of S^{-2} ion in the pyrite oxidation process (pyrite turns into goethite) may cause the precipitation of uraninite. This process is regulated by the sulfide

content of the host rock and by the possibility of bacterial development. Did these bacteria find a more adequate environment for development in the upper levels of an aquifer (or its rims) because CO_2 partial pressure was lower there than elsewhere? If the answer to this question is affirmative, then the distribution of uranium higher concentrations in the rock coinciding with horizons pigmented with red, reddish-brown and red-violet colours is explained, since the formation of such pigments is also favoured at the upper levels by a lower CO_2 partial pressure, as shown experimentally.

Furthermore, other phenomena must be taken into account to explain the process conducing to uranium concentration in the Atigradas sandstones. One of them is the possible reduction of U^{VI} to U^{IV} due to the action of the Fe^{+2} ion from the chlorites present in the host rock. Another process is U^{VI} fixation because of the sorption capacity of goethites produced from sulphur oxidation. It must also be remarked that the carbonatization of plagioclases is a SiO_2-liberating phenomenon which may give rise, in the presence of uranium solutions, to the formation of uranophane, another uranium mineral found in those rocks.

CONCLUSIONS

Recent detailed mineralogical studies (using X-ray diffraction, X-ray fluorescence, reflection microscopy, electron microprobe analysis, Mössbauer spectroscopy, etc) and chemical analyses (analyses of certain minor and trace elements) have confirmed the hypothesis stated in former papers (Nicolli, 1972; Nicolli et al., 1973) about the genesis of the uranium anomalies and ore bodies in the Sierra Pintada district.

From the successive consideration of the extraction from the source and transport process of uranium and the precipitation of uranium minerals in the host rock, it may be concluded that:

- The principal uranium sources are probably the tuffaceous rocks belonging to the Vieja Gorda Tuff Member and other volcanic rocks. They may have liberated uranium in the devitrification processes of the original vitreous material. Lesser amounts of uranium may have contributed the volcanic glass contained in the lithic sandstone fragments.

- The leached uranium entered the groundwater cycle which redistributed it. That process was facilitated by the dissolved CO_2 which increases uranium solubility by formation of the UDC and UTC complexes.

- The uranium bearing solutions circulated as free aquifer through the Atigradas sandstones when the lack of consolidation (incipient diagenesis) assisted that process.

- When oxygen became available, the oxidation of iron took place and it precipitated as γ-$Fe_2O_3.H_2O$ (lepidocrocite) only at aquifer upper levels, where the CO_2 partial pressure was lower.

- All laboratory experiments performed up to the present confirm the hypothesis of the existence of physico-chemical phenomena which, as a function of the CO_2 partial pressure, regulate the distribution of the reducing agents.

- Therefore, the action of the bacteria was only limited to the higher levels and rims of the free aquifer in the precipitation zone. Bacteria found there the most adequate environment for their development thus giving rise to a reduction zone where UO_2 precipitated. A remarkable fact is that the uranium ore horizons and the base of the phreatic water are parallel.

- The variations of the upper level of the water table caused with time the formation of more than one uranium ore horizon.

- Cross-bedding, as well as the different degrees of permeability in the host rock, only had ancillary importance in the distribution of the uranium ore.

- Other secondary factors in the distribution of the uranium minerals were: the presence of minerals of the chlorite series (which can liberate Fe^{+2}), the presence of sulphides (which by oxidation may give goethite) and carbonatization phenomena of the plagioclases which, upon the liberation of SiO_2, may give rise to the formation of uranium silicates.

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APPENDIX

BRIEF PETROGRAPHIC DESCRIPTIONS

1. Sandstones (Atigradas Sandstones Member)

These are arkoses, using this term in a general sense (total feldspars >15%). They present medium size grains and some horizons with fine and coarse grains. Colour is grey, pale grey or rose grey, but in some places the rock presents red mottles due to pigmentation with ferric oxides; this has given rise to the term "Atigradas" (tiger-spotted) sandstones. Sphericity (determined by microscopic study) is good to medium, and roundness is mainly subangular for the finer levels and subrounded for the coarser ones.

These rocks are characterised by lithic clasts of volcanic origin. Plagioclases (oligoclase-andesine) prevail over orthoclase. A weak kaolinization is rather extended, sericitization is not very important and chloritization appears with various degrees of intensity; carbonatization is a typical alteration process which mainly affects feldspars in various degrees ranging from weak partial attacks to complete clast replacement in some of the samples studied. Quartz is almost clean and shows fractured crystals. Perfect bipyramidal crystalline forms evidence effusive rocks at the source. Apatite and zircon are common accesory minerals.

Matrix composition is similar to that of the coarse fractions. Its alteration is mainly argillaceous and similar to feldspars alterations, that is, rather intense carbonatization and chloritization and weak sericitization. Minor amounts of organic matter (<0.1%) show irregular distributions in the matrix. Scarce cementing material composed by recrystallized clay minerals and carbonates and minor amounts of sericite and silica have been observed. In red samples ferric oxides are an important cementing agent.

2. Tuffs (Vieja Gorda Tuff Member)

These are acid rocks, mainly of rhyodacitic composition, sometimes dacitic-rhyodacitic composition, with crystallolithic characteristics and porphyroclastic texture.

The grain size is variable with roundness from subangular to subrounded. The mineralogical composition is quartz, feldspars- major plagioclases (oligoclase-andesine) and minor potash feldspars (orthoclase and sanidine)-, biotite and lesser amounts of muscovite. Lithic fragments and opaque minerals are also present. The former are partially of volcanic origin and show hypocrystalline material which may have been produced by devitrification processes. Apatite and zircon are common accesory minerals. The matrix is a felsitic aggregate of acid composition with chlorite, carbonate and iron oxides.

Feldspars show argillation as well as sericitization, but the principal alteration process is carbonatization (sometimes complete). Matrix material is affected by these alterations in the same way as feldspars. In some cases quartz and micas also show carbonatization, but in quartz and biotite the typical alteration is argillation. In addition, partial loss of iron is observed in biotites.

PLATE I

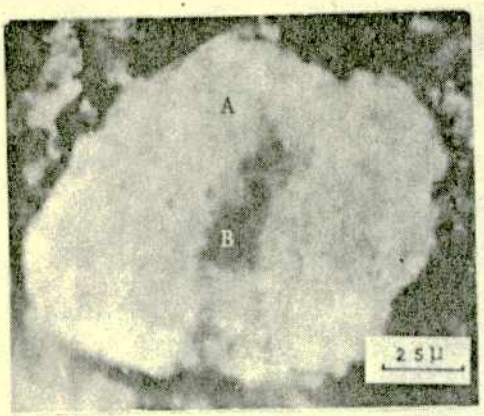
1, 2, 3: Microphotographs showing different degrees of pseudomorphosis of brannerite (B) after anatase (A).

4: Microphotograph of uraninite (U) in association with coffinite (C).

5: Ti X-ray image (250-250 μ).

6: U X-ray image (250 x 250 μ).

From Arcidiacono and Saulnier, 1979



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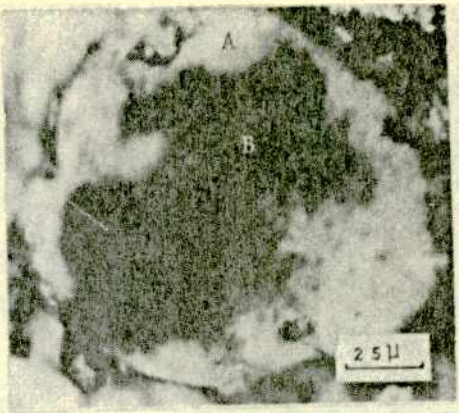

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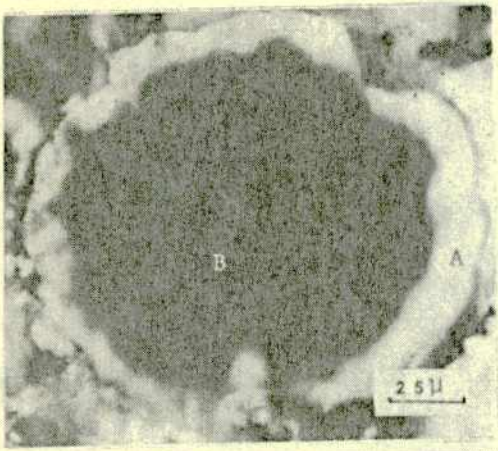

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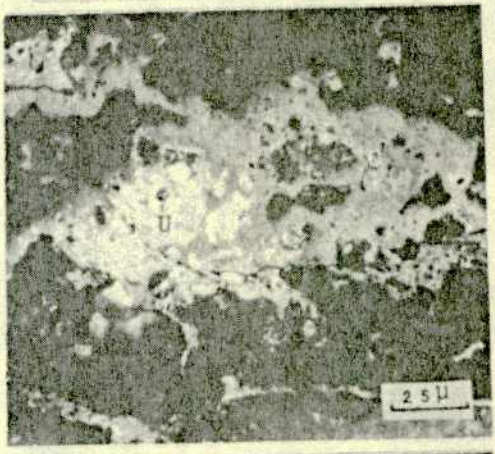

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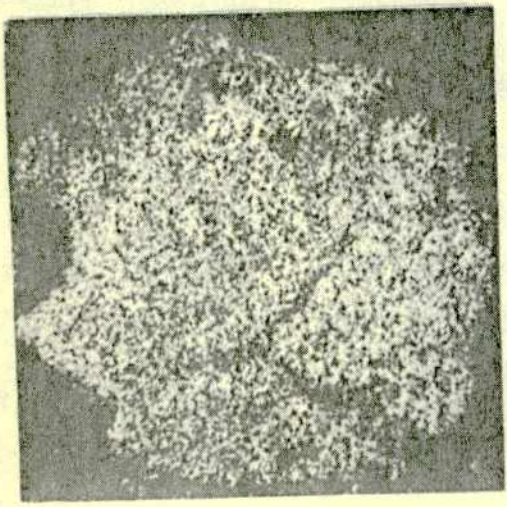
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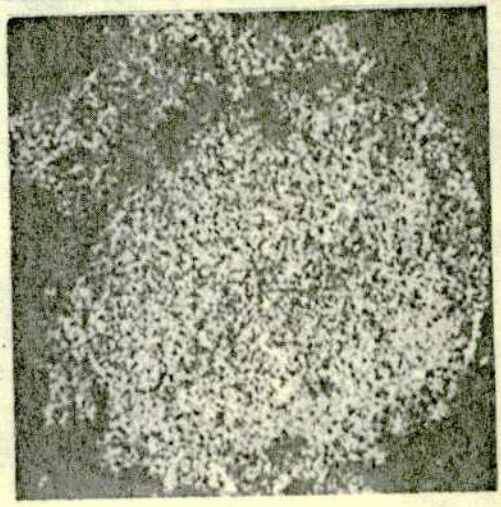
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