RADIOCOLLOID AGGREGATES IN URANIUM MINERALS

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ABSTRACT

Radiocolloid aggregates have been observed in the alpha ray pattern of altered uranium minerals. Properties of laboratory prepared radiocolloids suggest that the naturally occurring aggregates were probably composed of radium sulfate at the time of deposition. The radiocolloids exhibit at present an alpha ray activity about 50 times greater than that of normal uraninites. Their present day composition is essentially $Pb^{206}SO_4$ with about 0.003 per cent $RaSO_4$ as deduced from chemical and radiographic tests. This represents a 150-fold concentration of radium over that normally present in equilibrium with uranium.

INTRODUCTION

Radiochemical studies show that in dilute solutions of radioactive salts the solutes exist not only as individual ions, but also as discontinuous aggregates. These units have been designated radiocolloids, as they can be separated from the aqueous phase by centrifugation, dialysis and electrophoretic methods. The aggregates also exist in the gaseous state and have been observed by Harrington (5) during ultramicroscopic examination of radon tubes. The properties of the radiocolloids of the naturally occurring radioactive elements are described by Hahn (3) and Haissinsky (4). More recently, Kurbatov (7) has shown that this phenomenon also exists in solutions containing synthetic radioactive isotopes of the lighter elements. It permitted the isolation of radioyttrium from the solution of a deuteron bombarded strontium oxide target without the aid of a carrier.

The presence of atomic aggregation is readily demonstrated by the photographic method devised by Chamie (1, 2). The decay of isolated atoms is recorded by the silver bromide emulsion as individual tracks. Where aggregation exists, the developed pattern consists of a black core surrounded by a halo of radiating tracks produced by alpha particles striking the emulsion at glancing incidence. Structures typical of radiocolloid aggregation are exhibited in prints A and B of Fig. 1, showing microscopic details of the alpha ray pattern of a polonium film deposited electrolytically from acid medium on a copper disk.

RADIOCOLLOIDS IN URANIUM MINERALS

Microscopic examination of alpha ray patterns (10) from a series of polished sections of a single crystal of uraninite externally altered to gummite revealed minute structures of unusually high alpha ray activity in the altered portions, particularly the crystal tip (Fig. 2, *D*). Comparative photomicrographs (Fig. 1, *C* and *D*) of the alpha ray patterns produced by the gummite and the polonium film show a striking similarity in form. The radiographic images of the aggregates in the gummite range between 30 and 170 microns in diameter but the structures in the mineral are undoubtedly smaller as the image is enlarged by scattered and oblique alpha radiations. The gray background (Fig. 1, *D*) produced by the normal alpha ray activity of the gummite matrix obscures the finer detail of the halo, but furnishes a comparative basis for demonstrating the intense activity of the aggregates.

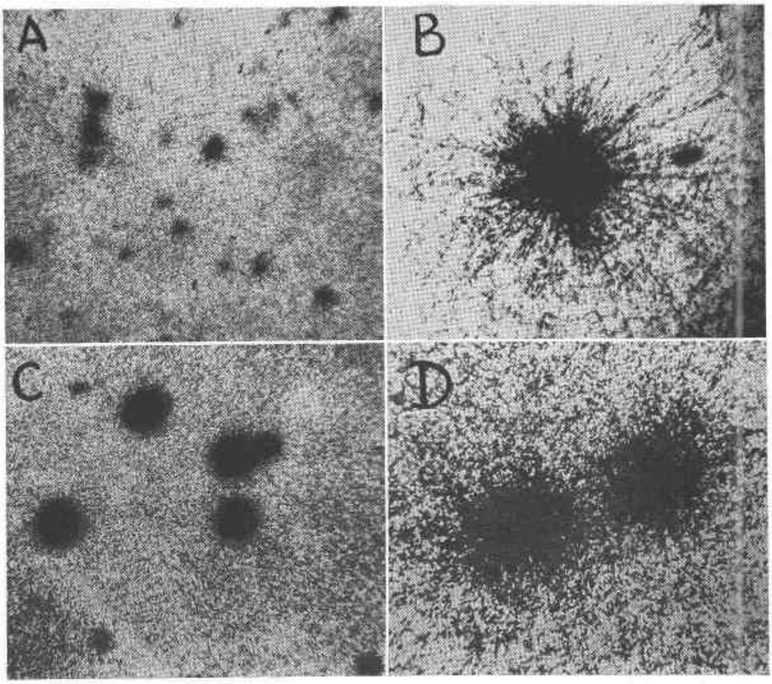

FIG. 1. Comparison of Laboratory and Native Radiocolloid Aggregates.

(*A*) alpha ray pattern of polonium film (38×) showing dark aggregates on a background of individual tracks from decay of polonium atoms.

(*B*) Single polonium radiocolloid at 280× showing tracks in halo.

(*C*) Radiocolloids in alpha ray pattern of gummite (38×) revealing several small aggregates comparable with those in print (*A*) and larger units usually not encountered in laboratory preparations.

(*D*) Radiocolloids in gummite at 200×. The fine detail of the halo is obscured by background alpha radiation from the matrix.

Study of Plate 1 shows that the individually resolvable radiocolloids have no visible point counterparts on the mineral surface, suggesting that the radiation emerges from units held in solid solution by the matrix. The macro regions of high alpha ray activity conform, in part, with the position of fine fissures on the polished section. These structures may contain radiocolloid aggregates in too close proximity for radiographic resolution. The point images correspond either to minute spheres or fine veins of radioactive matter intersected at right angles by the cutting plane. The former structure seems more probable, as the removal of about 100 microns thickness by repolishing causes the disappearance of the original point aggregates in the new pattern, whereas the fissure depositions persist. Also, the individual radiocolloid structures are rarely observed, while the fissure type of deposition is of frequent occurrence in altered uranium minerals, particularly along an interface. A striking example of such deposition on a border between uraninite and uranophane is shown in Fig. 3.

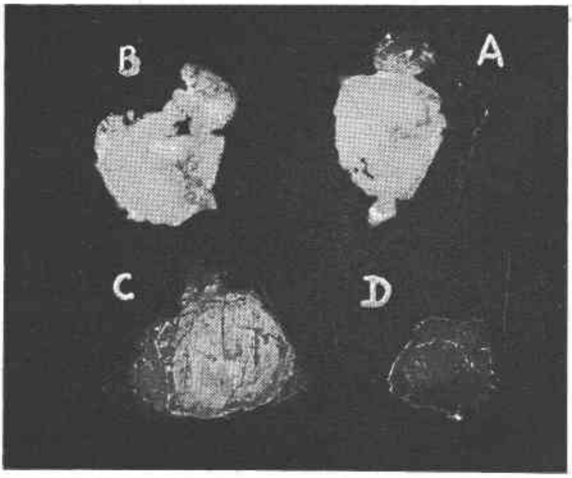

FIG. 2. Alpha Ray Pattern of Serial Sections of Altered Uraninite Crystal. Positive print (1×). Crystal from Brush Mineral Collection, Yale University. Found in a pegmatite located in Colombia, S. America.

(*A*) and (*B*) shows unaltered uraninite with several minute internal fissures.

(*C*) Pattern shows residual core of uraninite (gray) surrounded by alteration products.

(*D*) Apex of crystal completely altered to gummite. Note segregated regions (white) which exhibit an alpha ray activity exceeding unaltered uraninite (*A*) and (*B*).

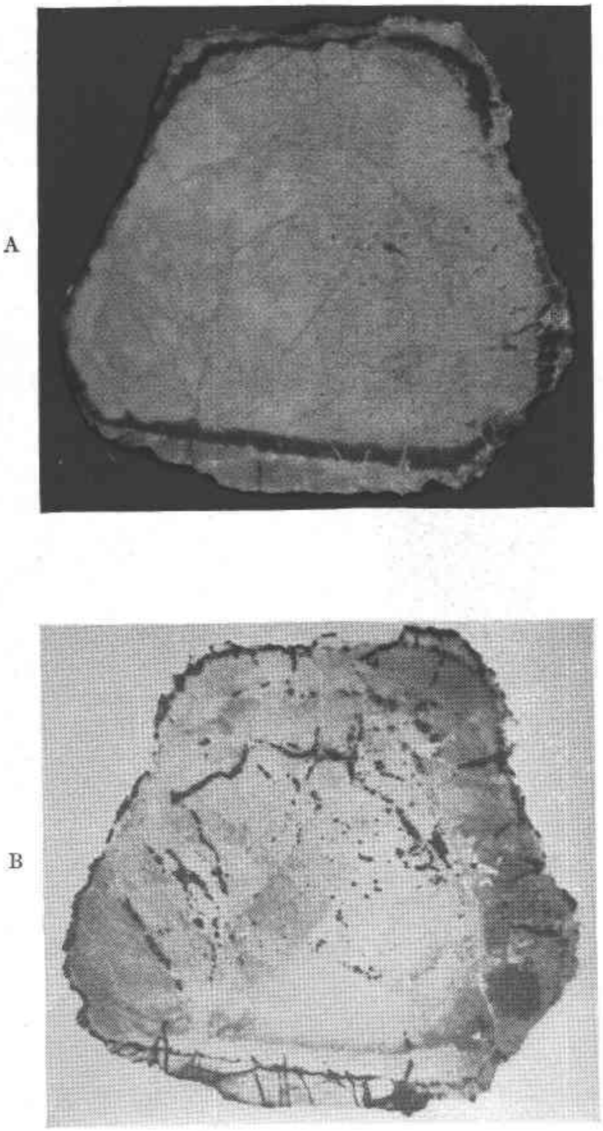

Plate 1. Comparison of Polished Gummite Section and Its Alpha Ray Pattern.
(*A*) Macrograph (5×) of gummite under oblique annular illumination.
(*B*) Macrograph (5×) of alpha ray pattern.

Examination of available patterns revealed the presence of individually resolvable radiocolloids in only three additional polished sections. These occurred in autunite from Mt. Painter, South Australia (U. S. National Museum 91921), a pitchblende from Shinkolobwe, Belgium Congo (U. S. National Museum 104784) and in a quartz-pitchblende section from Great Bear Lake, Canada (U. S. National Museum R-6736). Examination of the alpha ray patterns furnished by primary thorium minerals (monazite, thorianite and thorite) failed to show the presence of radiocolloid aggregates.

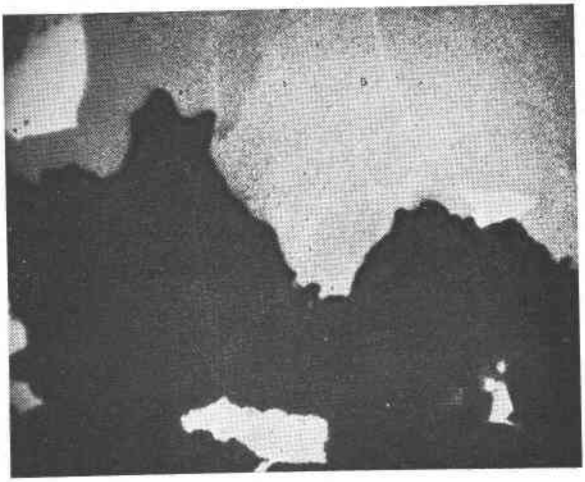

FIG. 3. Deposition of Radiocolloids Along Interface. Detail from alpha ray pattern (10×) showing zone of radiocolloid deposition (black) between uraninite (dark gray) and uranophane (light gray). The white inclusions are cyrtolite whose feeble radioactivity is not reproduced in the print. The zone of high alpha ray activity is revealed as a fine line of lead dithizonate on the ammonium acetate-lead pattern. Specimen collected by author at Spruce Pine, Mitchell Co., N.C.

The pattern produced by the Great Bear Lake pitchblende proved of particular interest as some of the radiocolloids were deposited in the quartz veins between the colloform structures of the pitchblende and these produced images unobscured by background radiation. The halo in the radiocolloid reproduced in Fig. 4 contains alpha ray tracks having a range in the emulsion of 53±2 microns. This is equivalent to an air range of 6.8±0.2 cm. and identifies the tracks as originating from RaC′. The core has an apparent diameter of 150 microns. Close examination of the same area on the polished surface did not reveal a black pitchblende inclusion of comparable size. However, the quartz showed an iridescent halo of about 90 microns diameter at the correlating point. Since the range of RaC′ alpha rays in quartz is 37 microns, and the iridescent halo probably corresponds to the terminus of the alpha ray track, the diameter of the radiocolloid aggregate is estimated at about 15 microns.

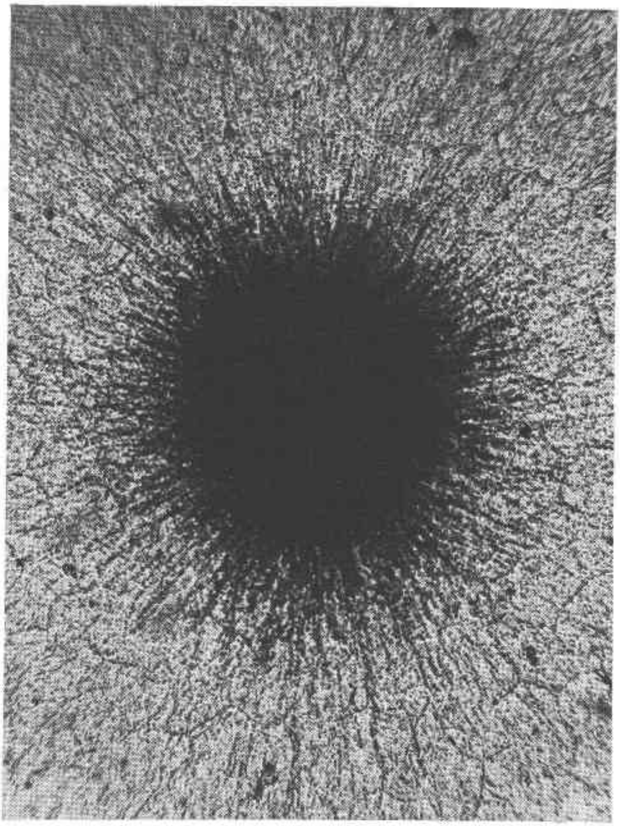

FIG. 4. Radiocolloid Aggregate Deposited in Quartz Adjacent to Pitchblende. Photomicrographic detail at 550× (reduced ½ in reproduction) from alpha ray pattern of Great Bear Lake, Canada pitchblende.

POSSIBLE ORIGIN OF THE RADIOCOLLOIDS

The radiocolloids deposited in the quartz are apparently unassociated with any parent uranium mineral. Examination of the polished surface under oblique annular illumination at the points corresponding to the location of the aggregates do not reveal particles with the color of pitchblende or its colored alteration products. Under vertical illumination with polarized light the points of high alpha ray activity are revealed by a reflectivity intermediate between the pitchblende and that of the quartz. The white particle enclosed in the inscribed rectangle (Fig. 5, *A*) corresponds to the geometric center of the radiocolloid image in the alpha ray pattern, *B*. Under higher magnification (Fig. 5, *C*) the point of origin is resolved into an apparent capillary structure of smaller circular areas having diameters between 1–2 microns.

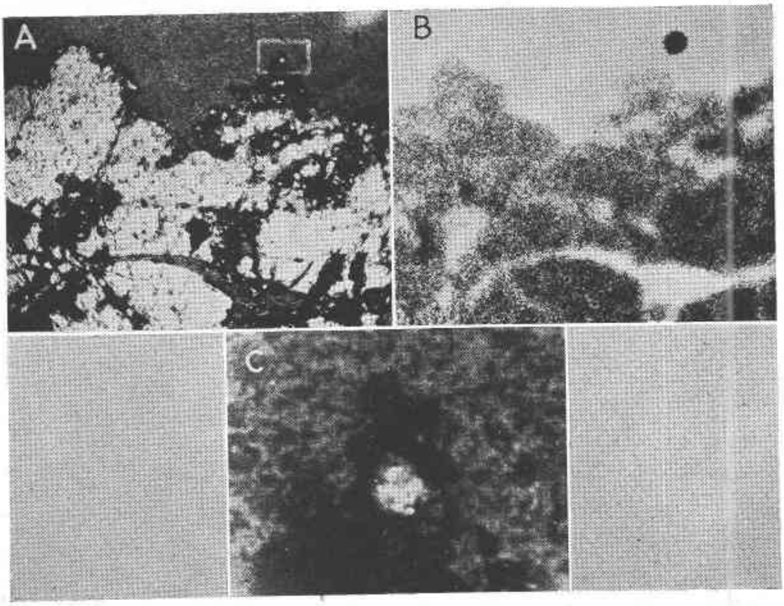

FIG. 5. Orientation of Radiocolloid in Polished Section.

(*A*) Photomicrograph (41×) of Great Bear Lake, Canada pitchblende under vertical illumination, showing pitchblende (white), quartz (gray) and altered pitchblende (black).

(*B*) Photomicrograph (41×) of corresponding area of alpha ray pattern.

(*C*) A 7× enlargement of point in polished section producing radiocolloid image.

The measurement of the photographic density of the radiocolloid images is rendered difficult by their minute size and extreme blackness. The alpha ray activity can be approximated by counting the RaC′ tracks in the halo and assuming that the resolvable tracks represent 5/90 of the total directed towards the emulsion. The radiocolloid reproduced in Fig. 4 contains about 100 tracks in the halo whose length is indicative of RaC′ origin. Thus, during the 100 hr. exposure producing the image, about 1800 RaC′ particles penetrated the emulsion accompanied by an equal number of rays from the decay of radium, radon, radium A and polonium. This corresponds to a P_α value of 16,000 per sec. per sq. cm., a value greatly exceeding that of the purest primary uranium minerals ($P_\alpha = 338$), and considerably smaller than the rate of emission from equilibrated radium sulfate estimated at 5×10^8 per sec. per sq. cm.

The abnormal rate of decay of the radiocolloid areas is explicable on the assumption that a substantially pure radium compound deposited in the capillaries, which decaying in the absence of regenerating material, diminished in abundance to correspond with the observed intermediate rate of disintegration. The initial formation of micro inclusions of radium sulfate can be explained in terms of two well established properties of radiocolloids. First, that the aggregates form at extreme dilutions far below the saturation point of the insoluble salts of the same composition, and secondly that the radiocolloids are readily adsorbed on porous materials. The latter property is particularly exhibited by dilute solutions of radium sulfate (saturation concentration at 20° is only 1.4 mg. per liter) which on passage through filter paper deposit 98 per cent of the radium on the cellulose fibers (3).

Descriptions of the Great Bear Lake pitchblende deposits (6, 9) show the presence of sulfur minerals and that the exposed pitchblende veins weather readily. Surface waters containing traces of sulfuric acid dissolve the alteration products forming a dilute solution of the metallic constituents, including the uranium and the radium in equilibrium with it. In an acid solution containing sulfate ions, the radium would exist as radiocolloids of the acid insoluble radium sulfate. Since uranium is not known to form radiocolloids in acid media it will exist dissociated as uranyl ions. When the solution passes through fissures in the quartz the aggregates deposit on the walls of the capillaries producing a filtrate substantially devoid of radium. Whether this simplified picture describes the exact mode of deposition is conjectural, but that a mechanism exists for the separation of radium from uranium solutions is shown by the occurrence of hydrated uranium minerals, such as autunite, which are practically devoid of their normal alpha ray activity (10) on the surface of pegmatite rocks.

The radium no longer in equilibrium with uranium or ionium decays rapidly with the formation of radiolead. From the observed rate of decay of the radiocolloids, it is possible to estimate the approximate time of their deposition by means of the law of radioactive decay, $P_\alpha = P_\alpha^0 e^{-\lambda t}$. Assuming the initial composition to be radium sulfate free from ionium, the age of the radiocolloids investigated is about 20,000 years. Owing to the rapid rates of decay of radium and its equilibrium products, the present composition of the radiocolloids is essentially $Pb^{206}SO_4$ associated with about 0.003 per cent $RaSO_4$. This represents a 150-fold concentration of radium in the aggregates as compared with the radium in equilibrium with the uranium in pitchblende.

Radiocolloid formation is probably a fairly common phenomenon in pitchblende deposits. Regions of high radioactivity have been recorded by Spence (8) in autoradiographs of Great Bear Lake pitchblende, and highly radioactive veinlets and dots in the mineral have been noted by Kidd and Haycock (6). The writer has observed essentially the same phenomenon in two separate samples from the Katanga, Belgium Congo deposit, the radiocolloids occurring in the veinlets of the yellow alteration products permeating the pitchblende. Individually resolvable radiocolloids were also observed in sections prepared from a highly altered pitchblende from St. Just, Cornwall, England.

Lead Patterns of Radiocolloid Areas

If the radiocolloids are composed of lead sulphate, as deduced from the mechanism of their formation, it should be possible to confirm this composition by means of the solvent action of ammonium acetate on this compound. The sections exhibiting radiocolloids were pressed against gelatin paper moistened with $2n$-$NH_4C_2H_3O_2$ and after one minute contact the paper was treated in succession with the following solutions: 5 per cent K_2CrO_4 (1 min.), 5 per cent acetic acid (2 min.), water (5 min.), 0.1 per cent dithizone in 10 per cent KCN (30 sec.) and running wash water for 15 minutes. The pattern of the pitchblende (Fig. 6) showed the presence of extractable lead only on the areas bordering the quartz where the radiocolloids are concentrated. Comparative microscopic observations revealed red points of lead dithizonate coincident with points of high alpha ray activity and also groups of circular lead areas which had no equivalent counterparts of high photographic density on the radio-

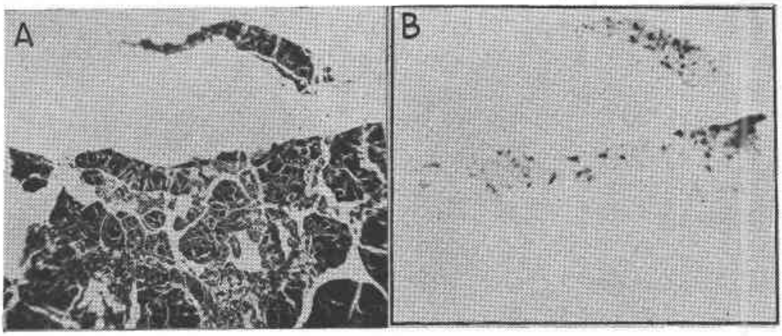

FIG. 6. Comparison of Alpha Ray and Extractable Lead Patterns of Great Bear Lake Pitchblende.

(*A*) Alpha ray pattern ($3\frac{1}{3}\times$).

(*B*) Ammonium acetate lead pattern ($3\frac{1}{3}\times$).

graph. The latter points probably correspond to older radiocolloids in which the radium has decayed to an activity comparable with that of the pitchblende. It is noteworthy that the unaltered pitchblende, holding about 10 per cent radiolead in solid solution, does not furnish an extractable lead pattern.

Tests on other polished sections showed that macro regions of abnormal alpha ray activity furnished a positive extractable lead pattern. The reaction is given by massive plumbian uranate minerals, such as curite and kasolite. Galena does not furnish a lead print by this mechanism. Ammonium acetate also exerts a solvent action on other sparingly soluble lead compounds and positive lead prints were obtained from polished sections of cerussite, $PbCO_3$, calcium larsenite, $(Pb,Ca)ZnSiO_4$ and pyromorphite, $3Pb_3P_2O_8 \cdot PbCl_2$. Thus, although the method is not definitive for lead sulfate, the absence of colored secondary inclusions in the pitchblende coupled with the insolubility of radium sulfate in acid solutions, limits the present day composition of the radiocolloids to lead sulfate. This printing procedure promises to be of utility in the study of the distribution of lead in radioactive minerals and further details will be presented in a report on the extractable and total lead patterns.

SUMMARY

The occurrence of radiocolloids in altered uranium minerals is not only of interest in showing a parallelism to a phenomenon known previously only in the laboratory, but their existence offers an explanation for the formation of zones of abnormally high alpha ray activity in minerals. A mechanism is described whereby radium is separated from uranium as a result of radiocolloid formation in acid media, and chemical evidence is presented identifying the lead resulting from the localized decay of the radium.

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