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POLISH ACADEMY OF SCIENCES  
INSTITUTE OF NUCLEAR RESEARCH

REPORT No. 1174

# PROPERTIES OF SEDIMENTS OF SPARINGLY SOLUBLE COMPOUNDS OBTAINED BY A VERY SLOW PRECIPITATION TECHNIQUE

by

Tadeusz Adamoki

W A R S A W

October, 1962

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ki, 11 p., p. 1136. Tel. 696-73; Nakład 700+7 egz.; UKPPIW  
HC/344/59. Zam. Nr 4/63. Oddano do druku 1.I.1963 r.

POLISH ACADEMY OF SCIENCES  
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PROPERTIES OF SEDIMENTS OF SPARINGLY SOLUBLE COMPOUNDS  
OBTAINED BY A VERY SLOW PRECIPITATION TECHNIQUE

O WŁASNOŚCIACH OSADÓW ZWIĄZKÓW TRUDNO ROZPUSZCZALNYCH  
OTRZYMYWANYCH TECHNIKĄ BARDZO POWOLNEGO STRĄCANIA

O СВОЙСТВАХ ОСАДКОВ ТРУДНО РАСТВОРИМЫХ СОЕДИНЕНИИ  
ПОЛУЧЕНЫХ ТЕХНИКОЙ ОЧЕНЬ МЕДЛЕННОГО ОСАЖДЕНИЯ

by

Tadeusz Adamski

Abstract

A new technique of very slow precipitation of sparingly soluble salts has been described. With the aid of this method sediments of crystallites of barium chromate have been obtained. The different shapes of the crystallites are supposed to be formed due to the presence of impurities of reagents, acting as specific crystallization centres.

A number of characteristic features have been observed and described, e.g. effects which are supposed to be radiation effects provoked by traces of radium in chromates.

### Streszczenie

Opisano nową technikę bardzo powolnego strącania osadów soli trudno rozpuszczalnych. Sposobem tym otrzymano osady krystalitów chromianu baru, których różne postaci przypisuje się obecności zanieczyszczeń w roztworach reagentów tworzących specyficzne ośrodki krystalizacji.

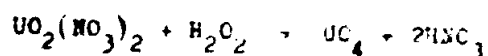
Zaobserwowano i opisano szereg charakterystycznych zjawisk, a m.in. efekty, które uważa się za uszkodzenia radiacyjne, a ich występowanie przypisuje się działaniu śladów radu obecnego w chromianach.

### Содержание

Описано новую технику очень медленно-го осаждения осадков трудно растворимых солей. Этим способом получено осадки кристаллитов хромата бария. Предполагается, что разные виды этих кристаллитов созданы благодаря присутствию разных примесей реактивов, действующих как специфические кристаллизационные центры.

Наблюдались и описаны характеристические явления а между этим эффекты, которые считаются радиационными повреждениями присутствии которых приписывается действию следов радия, присутствующего в хроматах.

Precipitation of sparingly soluble compounds is a frequent operation in the technology of uranium. For instance, it is employed with regard to sparingly soluble calcium, magnesium, and ammonium salts of polyuranyl acids, uranium dihydrotetrafluoride, uranium trioxide and tetroxide, and complexes of uranium with urea. Interesting is the very selective reaction of uranium tetroxide precipitation



which makes it possible to prepare uranium compounds of very high purity for nuclear fuels. In this reaction, the uranium tetroxide is obtained as a light-yellow sparingly soluble sediment. Usually though, it is amorphous, which does not promote separation of impurities. Another example of precipitation processes is purification of the waste waters of uranium ore concentration. The waters contain traces of uranium and derivative radioactive elements, the latter being removed by coprecipitation with accessory sparingly soluble salts. Precipitation of sparingly soluble compounds is a process frequently employed in chemical technology and is also of fundamental importance in analytical chemistry. The processes are usually very rapid and are as yet little known in spite of numerous studies.

From a list of the uses of these processes in only one technology, viz., that of uranium, it may already be seen that they are extensively applicable.

The quest for means of obtaining uranium compounds of very high purity with the aid of precipitation techniques has called attention to the fact that the parameter of time, which should be very important, is on the whole inadequately considered in work on precipitation. When the physics of these processes is contemplated it should be noted that precipitation yields rather large quantities of the solid phase within a relatively short time. It is possible for the solid phase to develop in either an ordered, crystalline, or a chaotic, amorphous form. For the ordered form to develop, a suitable period of time must be allowed. Furthermore, account

must be taken of the fact that the development of the solid phase is a process, in which successive amounts of the solid form first and foremost on the surfaces of the first-formed solid phase. Hence, the rate of precipitation should be adjusted according to the area of such surfaces, if new ones are not to develop spontaneously. Furthermore, ordinary conditions of precipitation make it impossible for an equilibrium between the developing solid phase and the liquid phase to become established, and also prevent an equilibrium in the solution itself in the case of more complicated reactions. Local conditions of concentration and pH may in some cases cause several solid phases to separate, even though only one should exist under the given conditions. In earlier, joint work with P. Macha [i] on the precipitation of neutral calcium arsenate, this was found to be attended by separation of the sparingly soluble arsenates



when precipitation was rapid, even though the reagents were added in stoichiometric proportions with reference to the tribasic arsenate. The equally known but little explored processes of coprecipitation might be explained similarly, it seems, assuming that foreign substances, either entrained mechanically or adsorbed on carrier formed surfaces, become covered by new layers of the substance precipitated and trapped firmly as impurities.

It appeared, therefore, that by adding the precipitant very slowly under vigorous stirring, and thereby slowing the formation of the solid phase, it should be possible to obtain purer and better crystallized compounds, which would filter and settle well. For the same reason the reagent should be added in a more diluted form in order to slow its introduction even further and prevent local strong supersaturations. Essentially, precipitation is crystallization and should also be assumed to involve conditions of metastable supersaturation (Miers's theory), which promote more ordered deposition of the solid phase owing to some delay in its formation.

A related subject has already been studied by P.P. von Weimarn [2,3]. He investigated precipitation of barium sulphate and the character of the precipitate in relation to the degree of the supersaturation of the solution. When very highly diluted solutions of sulphates and barium salts (0.00005 - 0.00017 N) are mixed no precipitate is formed, even though the solution becomes supersaturated for barium sulphate. With 0.0017 N solutions a precipitate is obtained within several seconds. When 0.0017 - 0.75 N solutions are used, the precipitates are composed according to von Weimarn of crystalline "skeletons", whereas still higher concentrations afford amorphous precipitates. R.B. Fischer investigated the effect of reagent concentration on the form of barium sulphate precipitates and particle size. He found that with very high dilutions of the reactants (0.0026 M) precipitates are obtained that pass through analytical filters (the particles are 4.3 microns in size), whereas more concentrated solutions (0.026M) yield crystallites 16 microns in diameter. Much research is devoted to methods of obtaining well-filtering precipitates of barium sulphate [5 - 10], a point important in analytical work. But in analytic chemistry emphasis is on the rapidity of precipitation, which in effect, though, does not meet the requirements referred to before. Another group of analytical research is concerned with the technique of homogeneous precipitation by precipitants produced "in situ" [11 - 22]. In this work, too, time is not a matter of concern and the reaction runs the full course within some scores of minutes at the most. Recommended analytical procedures specify only the solution temperature necessary for precipitation to be caused, e.g., by urea hydrolysis, and the actual reaction undoubtedly proceeds within a time appreciably shorter than that needed to heat the solution to the required temperature. The kinetics of precipitate formation was investigated many times and by various methods [8, 23 - 30]. But in these cases precipitation also took place with the usual velocity. Some authors recorded crystallites, their shapes being interpreted variously and attributed either to the concentration or the pH of the solutions [2, 5, 31 - 36]. Much like in the case of crystallization processes, considerable attention is devoted in this field to crystallization nuclei [37].



whose presence and role is inferred from studies on the kinetics of precipitation [24, 26, 30, 38 - 44]. The latter show that when precipitation begins, nuclei already exist, their size having been estimated in one of the studies at  $10^{-17}$  g. Closely associated with the problem of the precipitation of sparingly soluble compounds and at the same time of the purity of the precipitates is the phenomenon of coprecipitation, especially important in the purification of radioactive wastes. This is dealt by the school of Chlepin and in many of the publications listed in the Bibliography [47 - 72].

The new technique presently to be described of very slow precipitation, which has been developed on the basis of the briefly surveyed notions on the formation of the solid phase in precipitation processes, seems to lend itself well for detailed studies on the course of these processes and observation of some previously unknown phenomena.

**Apparatus.** The apparatus reproduced in Fig.1 represents the latest version developed in the course of the experiments. The fundamental element of the apparatus is the mixer, which consists of the glass tube (1), 25-40 mm across and roughly 800 mm long, to the bottom part of which is welded the capillary (2) as an air feed. The thinner tube (3), 6-10 mm across, is freely suspended on a thin platinum wire inside tube (1). When the apparatus is in operation, the air fed through the capillary (2) bubbles up through tube (3), causing the liquid in the apparatus to circulate intensively at a uniform rate. The bottom is suitably shaped to prevent sedimentation. The overflow (4) enables any excess of the solution to drain into the fraction collector (5), which is controlled by a clock-work so set as to cause the receiver vessel (6) to be changed hourly. The precipitant flows from the 1-litre Mariotte bottle (7) through the filter (8) and the limiting capillary (9) into the reactor (1). The orifice of the capillary (9) is immersed a little below the surface of the solution. The micropipette (10) serves for metering the flow of the reagent from the bottle (7). Before the apparatus is put in operation, the reactor (1) is

filled with a stock solution (so far a 5 % solution of  $K_2CrO_4$  was usual) and the air supply is turned on. Next, the cocks (11) and (12) are opened to release the precipitant from the bottle (7), the limiting capillary (9) being so chosen as to ensure the required flow rate at fully opened cocks. The flow rate can be metered with the aid of the micropipette (10); when the cock (11) is turned off the reagent continues to issue at the same rate, but only from the micropipette (10), and the flow velocity can be determined with the aid of a stop-watch. The reagent was usually a 0.05 percent solution of  $BaCl_2$  or  $Ba(NO_3)_2$ , and the flow rate, 0.2 ml/min. An assembly of six such apparatuses is shown in Phot. No.25.

In the first trials, carried out jointly with S.Rykowski [71], an apparatus built somewhat differently but on the same principles was used. In experiments with barium chromate used as a model substance for investigating the processes in point, precipitation with a diluted solution of barium chloride was found to yield solids composed of minute crystallites of the kind referred to by von Weismann as "crystalline skeletons" (Photos. 1 and 2). The crystallites had a strongly developed surface area owing to numerous dendritic ramifications; hence, this technique was unlikely to yield solids of high purity. Basically, however, the work showed there was justification for the view that the solid phase can develop in this process in a more ordered manner. Owing to the general importance of precipitation processes in the technology of uranium and other elements, the process was investigated more closely with the aid of the new technique outlined before. After the precipitation technique had been improved, the crystallites were noted to have an unusually symmetrical shape (Photos. 3 - 16), which was well reproducible (Photos. 9 - 10), and to settle readily. The present report describes some of the phenomena noted, an explanation of which will be given in subsequent communications.

Barium chromate, which was used as a model substance for studying precipitation processes, proved a very suitable material since it forms flat crystallites conveniently examined under

a microscope. Barium phosphate,  $Ba_3(PO_4)_2$ , yields under the same conditions three-dimensional crystallites in the form of four rods starting from a single point towards the vertices of a regular tetrahedron. Barium carbonate and sulphate also yield three-dimensional crystallites difficult to examine under an ordinary microscope.

The structure and symmetry of all crystallites indicates that growth began invariably from a single central point. Usually there is a distinct central body, which is undoubtedly the crystallite nucleus (cf. Photos. 11 - 16). If visible under the microscope, the nuclei have dimensions of the order of 0.1 - 1.0 micron, consequently also a mass of the order of  $10^{-12}$  to  $10^{-15}$  g and less. These dimensions approach those of the nuclei postulated by other authors on the evidence of studies on the kinetics of precipitation processes. The extraordinarily regular shape of the crystallites proves that the nuclei, too must be regular and symmetrical in shape. In some cases there is evidence of two-stage nucleation, with the symmetry of the larger nucleus clearly discernible (cf. Photos. 15 and 16). With a view to obtaining a confirmation of the visual observations and the view on the decisive role of nuclei in the growth of crystallites, experiments on the following lines were made. Barium chromate was precipitated during 24-48 hours from a solution of potassium chromate according to the technique and in the apparatus already described. The solid was filtered off, and precipitation was repeated. In this way a number of fractions of the precipitate were obtained, which differed from each other distinctly in character. As a general statement we may say that the first-formed crystallites are invariably much more diverse in form. The course of the phenomena observed during repeated precipitation from the same solution corroborate the surmise that crystallites form on nuclei, which consist of the natural impurities of potassium chromate. Identification of some of the nuclei will be dealt with further below.

Another important observation concerns the stability of the crystallites. They are rather resistant to mechanical action, and kept in a solution they undergo no recrystallization. Various

samples are kept in our laboratory since over four years, but no changes can be noted. The crystallites may be safely washed with pure water, dried, and stored. In this case too no changes can be noted, which shows that the crystal lattice produced is the most stable under the conditions described.

While the present work was in progress, another was started, jointly with R. Przytycka, on co-precipitation of radium and barium chromates. With the same idea on the formation of the solid phase in mind, the technique described in the present report was employed. In this case barium chromate was obtained in the form of simple straight prisms [72]. Inside these crystals there developed two, sometimes four symmetrically arranged spots (Phot. 17), considered first as gas bubbles, which eventually burst the crystal (cf. Phot. 18). Hence, barium chromate crystals probably form on nuclei provided by microcrystals of the less soluble radium chromate. In the course of radioactive fission, radium produces the so-called radiation damage, which gives rise to the observed "gas bubbles". In the earlier stages of the process, and probably also when the amount of radium is exceedingly minute, merely two dark dots are noted instead of the "bubbles". Owing to their characteristic appearance, this kind of barium chromate crystals are readily distinguished from others and identified (Photos. 19, 22, 23). They are now the subject of detailed investigations.

In the course of work on multiple precipitation of ordinary chemically pure potassium chromate, the removal of several fractions of crystallites was invariably followed by the appearance of the simple straight and characteristic prismatic crystals of the "radium" type, which showed evidence of similar radiation damage. This suggests strongly that the commercial "potassium chromate" reagent probably contains a minute amount of radium, possibly deriving from the chromite ore. For instance, industrial chromite ore (source uncertain) has been found to contain 0.0008 percent of uranium, consequently also a corresponding amount of radium.

In some experiments foreign ions, such as  $\text{Ag}^+$  and  $\text{MoO}_4^{2-}$  were added. With  $\text{Ag}^+$ -ions, characteristic shapes were obtained

which indicated the formation of double crystallites (Photos.20 and 21); with molybdenum, crystallites of an altogether different shape were obtained (Phot.8). The point whether these shapes are characteristic for molybdenum or the impurities in its compounds will be the subject of further investigations.

In microscopy, attention was attracted by the fact that crystallites similar in type are often found in clusters, even though the microscopic slide was prepared under conditions favouring uniform mixing of the crystals. The only possible interpretation of this phenomenon was that the particular nuclei, and subsequently the crystallites were formed on some basis binding similar nuclei. Investigations have so far shown that this base might be provided by organic substances (cellulose from filter paper or the products of cellulose destruction), the fibres providing such a base being invisible under the microscope. In other cases the base is provided by amorphous substances (e.g., hydroxides). If the precipitate thus produced is not removed, the crystallites continue to grow, producing eventually what is known in analytical chemistry as "flakes" (see Phot.24).

The investigations so far made have thus shown that:

- (1) considerable slowing of precipitation makes it possible to obtain crystalline solids.
- (2) the decisive role is played by nuclei, which consist of foreign substances.
- (3) different nuclei are not involved simultaneously but in a certain order of succession.
- (4) the method employed in the present investigations makes it possible to observe the process of nucleation and precipitation in stages.
- (5) the method employed enables the nuclei, consequently also impurities, to be eliminated gradually, and
- (6) the method enables the nuclei, consequently also traces of impurities to be identified.

The author is very much indebted to Mr Lech TROJANOWSKI for his patient aid.

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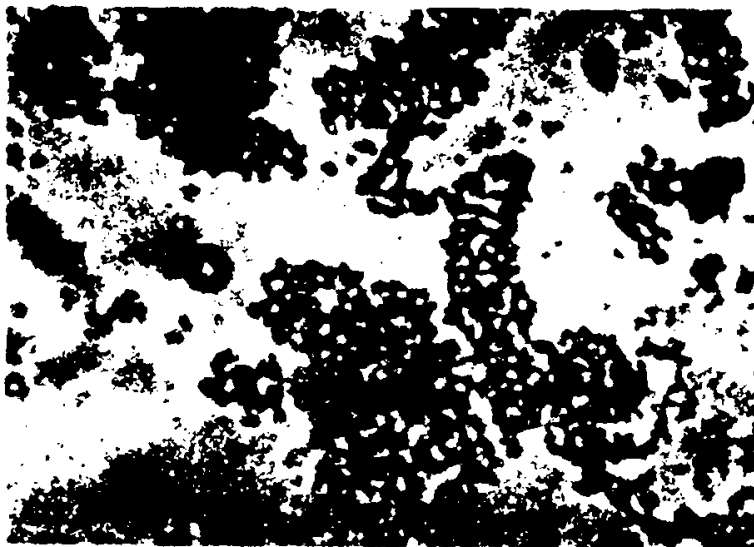
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Note : Photos No.4,7,8,9,11,14,15,17 and 18 have been  
performed by the author in the VEB-Carl Zeiss-  
Jena /East Germany/ laboratories by means of  
the/much indebted to VEB-Carl Zeiss for this  
kind assistance.



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Phot.1. Barium chromate obtained by  
conventional precipitation.



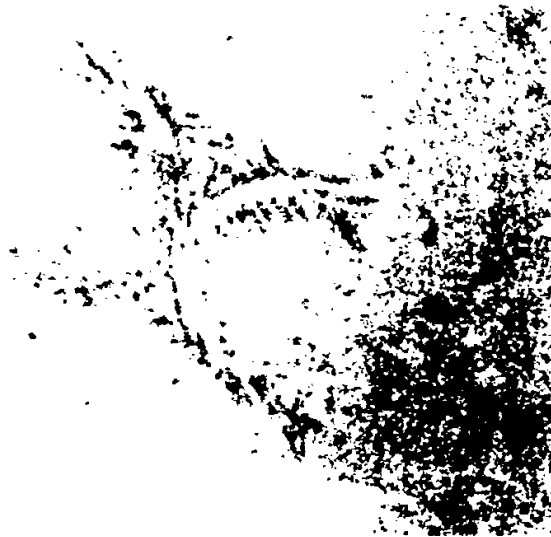
Phot.2. Barium chromate obtained by  
very slow precipitation.



Phot.3. Characteristic shape of the  
crystal.



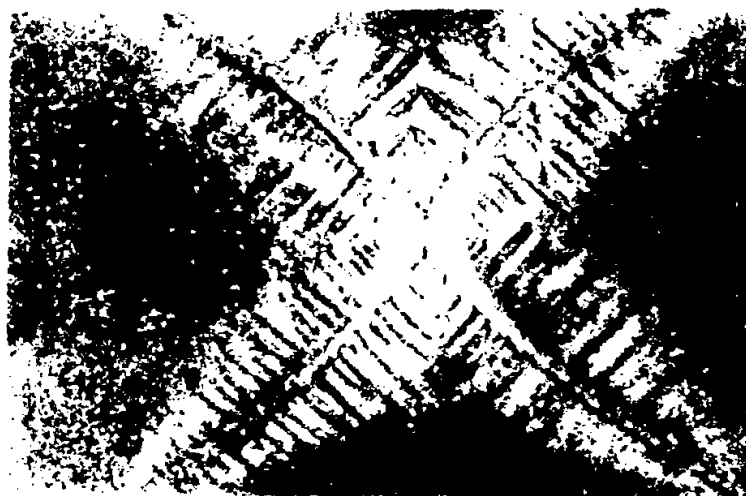
Phot.4. Characteristic shape of the  
crystal.



Phot.5. Characteristic shape of the  
crystal.



Phot.6. Characteristic shape of the  
crystal.



Phot.7. Characteristic shape of the  
crystal.



Phot.8. Characteristic shape of the  
crystal.



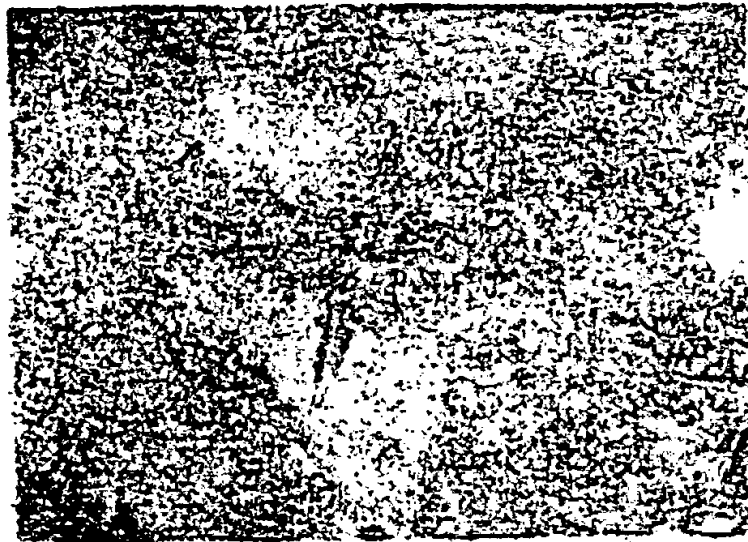
**Phot.9. The shapes are reproducible.**



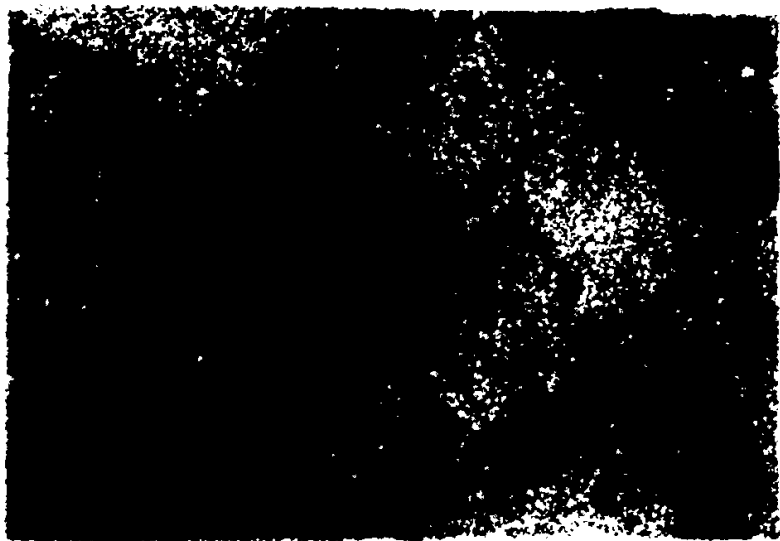
**Phot.10. The shapes are reproducible.**



Phot.11. Crystallite with nucleus.



Phot.12. Crystallite with nucleus.



**Phot.13. Crystallite with nucleus.**



**Phot.14. Crystallite with nucleus.**



**Phot.15. Crystallite with double nucleus.**



**Phot.16. Crystallite with double nucleus.**





**Phot. 17.** Barium chromate crystal with radium nucleus. Note the "radiation damage" caused probably by radium.



**Phot. 18.** Barium chromate crystal with "radium" nucleus. Note the "radiation damage".



**Phot.19. Barium chromate crystallites inter-  
spered with "radium" crystallites.**



**Phot.20. Mixed barium-silver crystallite.**



**Phot.25. Apparatuses.**

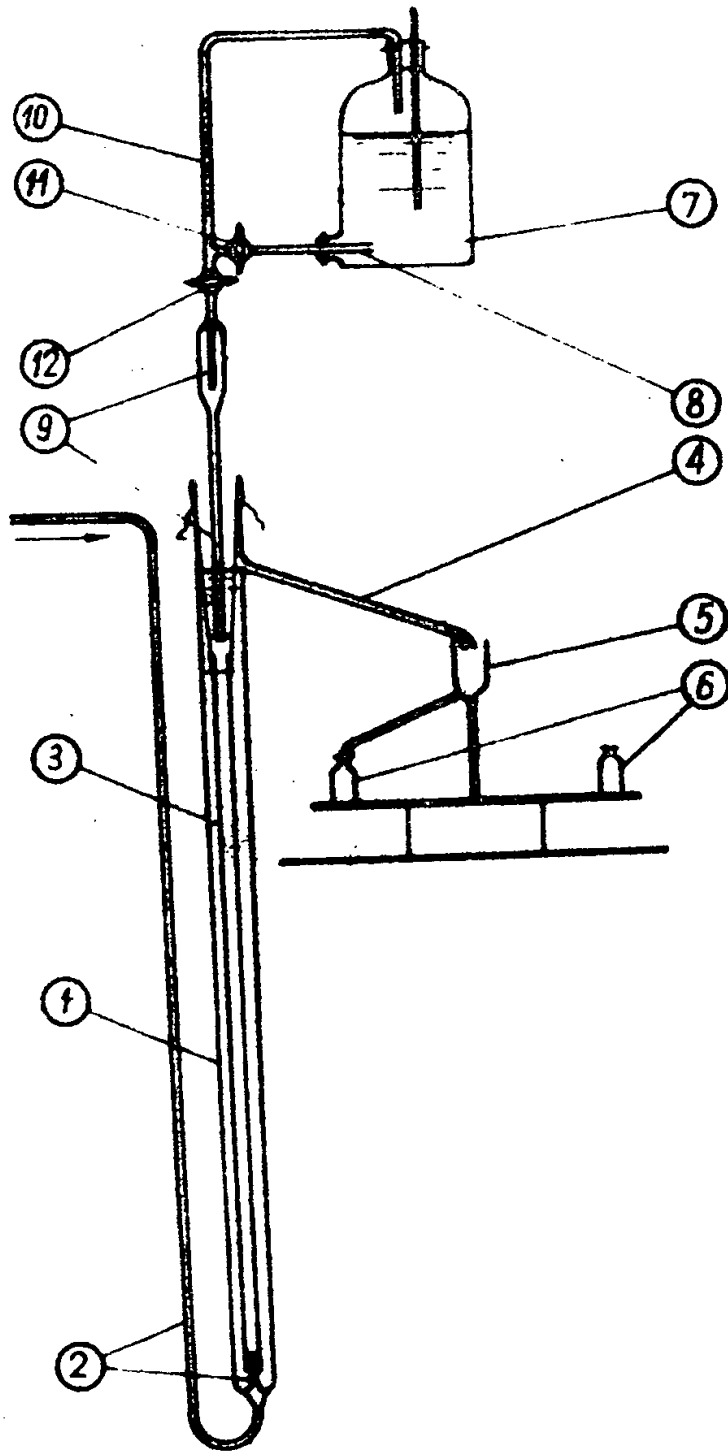


FIG. 1.

Ontario almost contemporary with the Blind River conglomerates, heavy mineral assemblages completely of modern aspect are widely developed, indicating that the mineralogy of the blanket ores cannot be explained in terms of abnormal atmospheric conditions. The latest work on the Serra de Jacobina ore-body shows clearly that this deposit is not alluvial, and that the mineralization was probably emplaced hydrothermally<sup>4</sup>. The recently discovered Russian deposits of blanket-type gold-uranium ores<sup>5</sup>, the locality of which has not yet been revealed, exhibit both sulphidic (pyrite, uraninite) and oxide (magnetite, brannerite) phases in the same conglomeratic ore-body, demonstrating beyond a shadow of doubt that the mineral assemblages are of hydrothermal origin.

The orthodox geological conceptions on the history of the atmosphere have recently been reviewed by A. P. Vinogradov<sup>6</sup> in his Vernadsky Memorial Lecture, in which he concludes that the primeval atmosphere of methane, hydrogen and carbon dioxide (akin to the gases of meteorites and of terrestrial rocks of mantle origin such as kimberlites, carbonatites and dunites) lasted only a relatively short time. Probably it was lost in the 1,000 million years of the Earth's history before the earliest known rocks came into being. A. A. Polkanov<sup>7</sup> has lately observed that even for those earliest Katarachanan rocks of 3,500 million years ago, Lyell's principle of actualism may not, and should not, be repeated.

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<sup>1</sup> Hermal, J. D., *Nature*, **196**, 850 (1961).

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<sup>3</sup> White, M. G., *Geothermal Survey Research 1961*, R. S. U. S. Geol. Surv., Washington (1961).

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<sup>5</sup> Vinogradov, A. P., *Khimicheskaya Evolyutsiya Zemli* Akad. Nauk Moscow, 1960.

<sup>7</sup> Polkanov, A. A., *Uspeniy Geokhimiya i Geologii* (Akad. Nauk Moscow 1961).

THE origin of early Precambrian gold-uranium ore deposits has indeed been a controversial issue. But, as I stated explicitly in my book, I have become convinced that the features acquired by hydrothermal processes are due to younger alterations. These deposits are placers originally. The hydrothermal alterations have been important in enriching the original placers. They may even be at the origin of the money value of a given deposit, and consequently seen as the most important process by an economic geologist.

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## CRYSTALLOGRAPHY

### 1. Commination of Crystal Nucleation by a Precipitation Method

THERE are two ways to precipitate sediments of slightly soluble salts, namely, by simple mixing of the reagents or by the homogeneous method, that is, by developing the reagent *in situ* and thus precipitating the insoluble salt homogeneously in the whole bulk of the solution. In both cases no special care is taken with regard to nucleation and the parameter of time.

The formation of a sediment of an insoluble salt comprises two basic processes, the character of which is quite different: a chemical process involving the formation of a new compound of the ions existing in or introduced into the solution, and a physical process of solid phase formation. Different kinds of this general scheme, comprising extreme and intermediate cases, are being examined. The

some process of chemical compound formation proceeds very fast. The physical process is rather slow and thus, depending on existing conditions, the solid phase is obtained as an amorphous body, that is, of poorly ordered crystal lattice or in the crystalline, well-ordered state.

The principle of the new technique, which I have developed, is to perform the chemical reaction as slowly as is necessary to obtain a well-ordered solid phase, that is, a crystalline form of the sediment. Under such conditions many new features, unknown until now, have been observed.<sup>1,2</sup>

Now further work has revealed that

(1) Crystallization proceeds on nuclei of symmetric shape and a mass of only  $10^{-12}$  g or smaller.

(2) A great, but limited, number of crystallite shapes are obtained. The shape depends on the nucleus acting as a centre of crystallization.

(3) The different shapes are obtained simultaneously, which shows that just the specific properties of the nuclei are responsible for the shape and not the properties of the medium, for example, the concentration, surface tension, pH, etc. (Fig. 1).

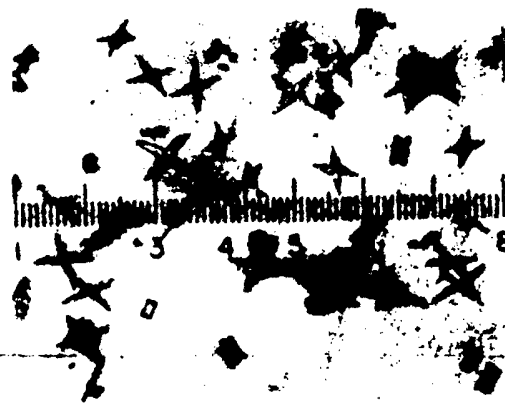


Fig. 1. x 400

(4) While introducing small quantities of foreign ions (the basic precipitate being barium chromate) crystallites of quite different shape are obtained. Because of the lack of separating methods it could not be established until now whether they were other compounds or other crystalline forms.

(5) A fractional precipitation performed with the aid of the new method removes the existing nuclei. On further precipitation the number of crystallite forms diminishes.

(6) In spite of their very delicate structure the crystallites are very stable. It has been stated that sediments do not change while in contact with the mother liquor for a period of even four years, showing that the solid phase has been formed under conditions enabling the building of an ideal crystal lattice, that is, a lattice of lowest energy.

(7) Observations have shown that nuclei formation proceeds possibly on amorphous matter of indefinite composition (hydroxides?, silica?).

I thank Mr. L. Trojanowski for assistance in performing the experimental work.

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<sup>3</sup> Adamski, T., and Przystycki, R., *Nucl. Res. Inst., Warsaw, Rep. No. 295*, 4 (1961).

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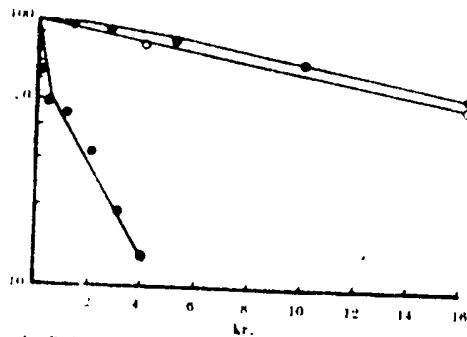


Fig. 1. Radiation effect on DNA as percentage of the control. (Open circles, viscosity of native DNA; closed circles, viscosity of the single-stranded DNA; half-filled circles, breaking of the hydrogen bonds; 0.05 per cent DNA in 0.01 M sodium chloride)

dose rate: 3,150 r/min). We also determined the amount of open hydrogen bonds in the native irradiated DNA according to a method described in an earlier article<sup>5</sup>. The viscosity of the native DNA and the hydrogen bonds between the two strands have nearly the same radiosensitivity; the  $D_{50}$  is about 30,000 r. After separation of the strands, however, the viscosity drops to 50 per cent after 500 r. The dose effect curve seems to have two components: one with  $D_{50}$  of 700 r, the other with  $D_{50}$  of 2,500 r. The two components of this curve may be discussed in a similar way as Latarjet *et al.*<sup>6</sup> did when considering the inactivation of the transforming factor in the DNA, where the  $D_{50}$ -values of the two components also have a ratio of 1 : 4 (1,000 and 4,000 kr.).

The breaks of the single strands are permanent in native DNA over a longer period. If the DNA is denatured only 24 h after irradiation of 500 r, the viscosity of the single strands decreases to 40 per cent of the control instead of 50 per cent. This means that there is a small 'after effect' of the irradiation.

If DNA is first denatured and then irradiated, the loss of viscosity is very small. After 1,000 r, no change of the viscosity was observed. The same effect has been described by Marmur *et al.*<sup>7</sup> after irradiation of DNA with ultra-violet light. The high sensitivity of the single nucleotide chain in native DNA might be explained by the fact that the target volume in the stiff double helix is larger than the target in the coiled single-stranded DNA.

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## RADIATION CHEMISTRY

### Possible Radiation Damage Effects in Barium Chromate Crystals

Barium chromate obtained by the method elaborated in our laboratory<sup>1, 2</sup> forms crystallites the shape of which depends on the kind of nucleus on which the crystallite has been formed. Under special conditions, for example, by fractional precipitation using the same method or by precipitation from dilute solutions, reagent grade potas-

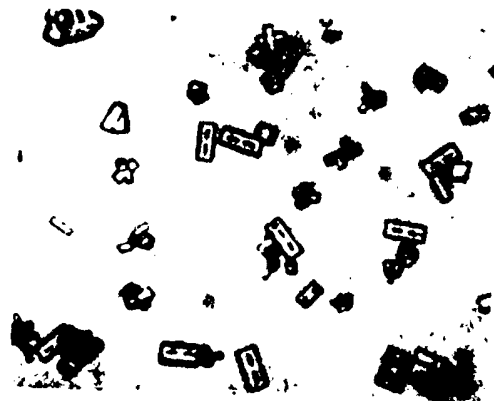


Fig. 1. x 400



Fig. 2. x 400

sium chromate produces sediments of prismatic-shaped barium chromate crystallites having a rhombic cross-section.

Very often it has been observed that two elliptical 'gas bubbles' inside the prisms were formed. Crystallites of smaller size show two 'funnels' on the ends, instead of the 'bubbles', while others show only two or four dark points (Figs. 1 and 2). A similar feature was observed by us earlier, while precipitating barium chromate from solutions containing uranium and radium<sup>3</sup>. Observations described elsewhere<sup>4, 5</sup> show that crystallites are formed on nuclei consisting of foreign substances. It is supposed that, in the case recorded here, barium chromate crystallizes on isomorphous radium chromate nuclei, traces of radium coming from uranium and thorium always present in chromite ores.

The radioactive decay of radium causes strong radiation damage effects similar to those described, for example, by Yoshida<sup>6</sup> and Vineyard<sup>7</sup>. The great energy of the decay as also the concentration of the source—that is, the crystal nucleus—produces effects sufficiently strong as to be visible by simple microscopical observation. Also it has been shown by us (by slightly levering the tube of the microscope) that the crystalline substance in the vicinity of the 'bubble' is of greater optical density and acts as a regular optical lens. These observations fit very well to the features of vacancies and interstitial formation as postulated for radioactivity effects in crystal lattices. The 'funnels' already mentioned have been observed on very small objects 5–7 μ long. This fact seems to be in accordance with a similar effect described for uranium metal by Rogers and Adams<sup>8</sup>.

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In some experiments crystallites showing radiation damage effects have been obtained, where no further changes could be detected. In other cases crystallites of exactly the same shape showed no effects of this type. Differences, as such, can be ascribed to the different sizes of radium chromate nuclei, or to different radium isotopes present, that is, radium 224 ( $t_{1/2} = 3.64$  d.), radium-226 ( $t_{1/2} = 1620$  y.) and radium 228 ( $t_{1/2} = 6.7$  y.). The strongest damage is expected to be caused by radium-224. Many other observations made are in good accordance with the interpretation of facts presented here.

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## CERAMICS

### A Simple Flame Fusion Apparatus

The need for large single crystals of refractory oxides has been ever increasing in recent years. In many instances further technological advances are being hampered by the lack of materials of suitable purity and perfection. One of the major sources of contamination of materials prepared at high temperature is the container in which the material is heated. The flame fusion technique is one high-temperature crystal growth method which overcomes the container problem as the material under investigation acts as its own support. A rather complete review of the advantages, limitations, and apparatus of flame fusion furnaces is given by Popov in a book edited by Shubnikov and Sheftal.

This communication describes a simple portable flame fusion apparatus which can be constructed in most laboratories with readily available materials.

The apparatus consists of three major components: (1) the feed hopper and burner assembly; (2) lowering mechanism; (3) the gas system. The usual feed hopper assembly consists of an outer and inner hopper. The inner hopper is fitted with a fine mesh sieve which is vibrated by a tapper mechanism for control of feed flow. A new design of a one-hopper feed assembly has been incorporated into a flame fusion apparatus. In this version continuous and uninterrupted feed rates are accomplished. The feed hopper is designed such that commercially available burner assemblies can be used and interchanged with ease.

The pedestal on which the crystal is grown must be lowered at a rate equal to the growth rate of the crystal. In addition the rate of lowering must be variable to coincide with slow or rapid crystal growth. It is also very important that the lowering mechanism transmit as little vibration as possible to the growing crystal. A compact and versatile lowering mechanism was designed to eliminate the difficulties usually encountered. A variable-speed d.c. motor and a gear train system permit the growing boule to be lowered in the continuous range from zero to 4 in. per h. The lowering mechanism is equipped with an independently variable rotation mechanism which can rotate from a fraction to 100 r.p.m. by suitable choice of gears and motors. The housing for the lowering mechanism is shock mounted and can be positioned by means of a two-dimensional slide rest. A schematic diagram of the lowering and rotation mechanism is shown in Fig. 1.

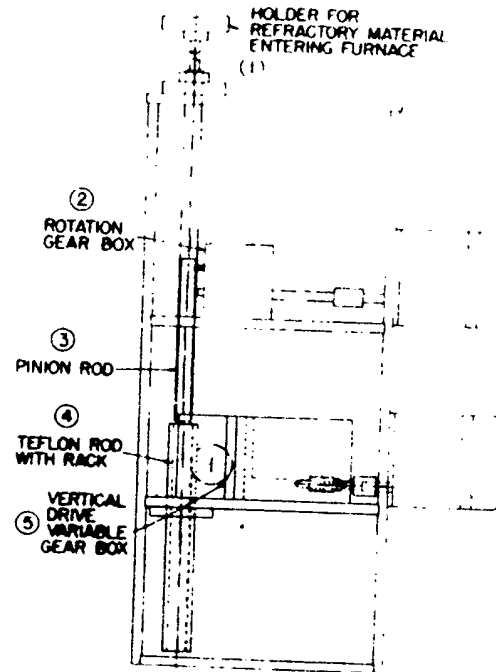
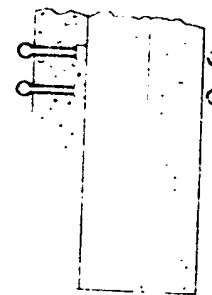
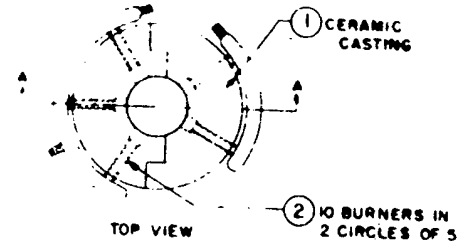


Fig. 1. Lowering mechanism.



SECTION A-A  
Fig. 2. Annealing furnace.

A refractory furnace muffle with tongue and groove joints was cast from 33 HD alundum (Norton Refractories, Worcester, Mass.) to contain the heat source. An adaptation of this muffle has been designed as an annealing furnace to reduce the strains in growing boules by *in situ* annealing. This furnace consists of two rows of five burners each using oxy-hydrogen gas. The burners are positioned and the manifold cast in a refractory muffle as shown in Fig. 2.