

## BASE EXCHANGE IN ARTIFICIAL AUTUNITES.<sup>a</sup>

J. G. FAIRCHILD, *U. S. Geological Survey.*

### INTRODUCTION

BY W. T. SCHALLER

Some years ago, while relating to Prof. A. N. Winchell, of Madison, Wisconsin, the results of readily hydrating and dehydrating autunite with the formation of definite hydrates with characteristic optical properties,<sup>1</sup> he raised the question as to whether or not the calcium in autunite could be replaced by other bases, with similar ease. Mr. J. G. Fairchild was at that time making artificial pyromorphite by a "salting out process" and kindly undertook the problem of making artificial autunite by the same process. Using sodium chloride as the "salting out" reagent, a well crystallized product was obtained, which to our surprise was found on analysis to contain only a little calcium and much sodium. As such a result strongly indicated that the base exchange reaction, as suggested by Winchell, was feasible, Fairchild agreed to undertake the necessary laboratory work and analysis, and to find out whether or not the calcium in autunite could be readily replaced by other bases. As both the calcium and the sodium artificial autunites could be prepared in quantity with ease, all the work was done on such artificial material.

The results, given below, show that such base replacement takes place very readily and that a large number of such different artificial autunites can be made. Starting with an artificial calcium autunite, all the calcium was readily replaced by sodium; starting with an artificial sodium autunite, the sodium was readily replaced by calcium, potassium, barium, manganese, copper, nickel, lead, and magnesium. With lead the end product was neither homogeneous nor well crystallized and the lead percentage was too high. A lead autunite was, however, successfully made by another method.

These experiments show that base exchange reactions take place very readily with compounds of the autunite type. All of the products obtained, with the exception of the lead-containing replacement product, were tetragonal plates four or eight sided, both uniaxial and biaxial, which had values for the refractive indices concordant with those found for the corresponding natural minerals.

Like so much of the natural autunite, some plates were isotropic when lying flat and birefringent when turned up on edge, whereas other plates showed a weak and irregular birefringence in the basal plates. No quantitative refractive index measurements were made consistently on any of these samples at the time they were analyzed; neither were they determined where the material was under known hygroscopic control. In fact most of the determinations were made several years after the material was analyzed but on material from the same tube from which the sample analyzed was obtained. A few check determinations, however, showed that no material change in the water content of the samples had taken place.

Like the natural autunites and other minerals of this same group, all the artificial preparations were optically unhomogeneous, a result probably due to the

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<sup>1</sup> The paper giving these results is in course of preparation.

presence of more than one hydrate in the sample.<sup>2</sup> The following optical varieties have been noticed in the artificial preparations, often all in one sample, and frequently several varieties form parts of a single crystal.

- (1) Strictly isotropic basal plates, uniaxial, negative.
- (2) Biaxial, weakly birefringent on basal plates.
- (3) Biaxial, strongly birefringent on basal plates.
- (4) Polysynthetically twinned, the lamellae being parallel to (100), or (110); or both.

The value of the axial angle also varied considerably on different crystals of the same sample.

#### METHODS OF PREPARATION

Several attempts were made to prepare artificial autunite in distinct crystals. The first attempt was made by boiling a solution of the nitrates of uranium and calcium with a solution of phosphoric acid. The resulting product was very fine-grained and apparently not homogeneous. The time element was then introduced and it was found that a well crystallized product could be obtained in a month or so by allowing a solution of uranium and calcium nitrate to mix very slowly with phosphoric acid by diffusion through a large volume of water. The first precipitate formed had an amorphous appearance but by leaving it undisturbed for a month or more, relatively large sized plates of well crystallized artificial autunite were obtained. While awaiting the outcome of this procedure, the method suggested by McDonnell and Smith<sup>3</sup> was employed, namely of precipitating the desired compound by a "salting out" process, using a strong solution of sodium chloride. Quite unexpectedly, the resultant crystals of artificial autunite, when analyzed, showed only about one-sixth of the required quantity of calcium. Tests soon showed that considerable sodium was present and quantitative analysis showed that these crystals were essentially the sodium equivalent of the calcium-uranium-phosphate.

In this "salting out" process, the action of the sodium chloride brine may be twofold; first, a reduction of the hydrolytic effect

<sup>2</sup> A study (unpublished) of natural autunite has shown that the variation in optical properties of autunites and the apparent inconsistency of their optical character as related to the geometrical form, is due chiefly to the existence of several hydrates whose stability range (at room temperature) is dependent on the vapor pressure of the surrounding air.

<sup>3</sup> McDonnell, C. C., and Smith, C. M., The preparation and properties of lead-chlor-arsenate, artificial mimetite. *Am. J. Sci.*, 4th ser., 42, pp. 139-145, Aug. 1916.

of the water, second, a repression of the solubility of the phosphate formed. The starting point was a solution of one gram of di-calcium phosphate dissolved in just enough dilute hydrochloric acid. It was later found that the same result was obtained by mixing solutions of calcium chloride and of phosphoric acid in the correct proportions to form the di-calcium phosphate. This phosphate solution was then added to a nearly boiling solution of sodium chloride (150 gms. NaCl to 500 c.c. H<sub>2</sub>O). There was then added the precipitating agent (3.7 gms. UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O dissolved in a little water), which contained the necessary quantity of UO<sub>3</sub> for the formation of the compound CaO·2UO<sub>3</sub>·P<sub>2</sub>O<sub>5</sub>·8H<sub>2</sub>O. A small excess of uranium is not harmful. No precipitate should form at once. If the gradual addition of the uranium salt does cause an immediate precipitation, a little dilute hydrochloric acid is added to clear the solution before the addition of the bulk of the uranium salt. As this mixture slowly cools to room temperature yellow platy crystals of appreciable size appear.

That the degree of acidity is one of the factors controlling the size of crystals is shown in the formation of the sodium autunite. Crystals of the calcium variety were placed in a solution of sodium chloride to which hydrochloric acid was added in just sufficient quantity to dissolve these crystals. The acidity was then reduced by gradual addition of sodium carbonate dissolved in a little water to the point of re-precipitation. The volume of liquid was then increased to three liters by addition of water. As this volume of liquid stood for some three months exposed to slow evaporation at room temperature, crystals of sodium autunite were produced in size appreciably larger than in the early experiments. The clear liquid was decanted and the crystals washed free from sodium chloride. When examined under the microscope, they appeared wholly crystalline and homogeneous and showed well developed rectangular and 8-sided yellow plates similar to those of natural autunite.

An analysis of the air-dried crystals, obtained by "salting out" supposedly the calcium compound by the use of a sodium chloride brine, showed the somewhat surprising result that only about one-sixth the quantity of calcium belonging to autunite was present. The remaining five-sixth was sodium. Such a base exchange might have been expected, however, in view of the experience of Hille-

brand<sup>4</sup> who found that the calcium and potassium in the carnotites were mutually replaceable with ease.

#### ARTIFICIAL AUTUNITES PRODUCED

The crystals first obtained from a NaCl brine by the "salting out" process, had the following composition:

##### ANALYSIS OF THE CRYSTALS FROM NaCl BRINE.

	Per cent	Ratios
P <sub>2</sub> O <sub>5</sub>	16.13	.114 or 1
UO <sub>3</sub>	64.90	.227 or 2
CaO	1.10	.020
Na <sub>2</sub> O	5.62	.091
H <sub>2</sub> O (ign.)	13.22	.734 or 6.5
	100.97	

These ratios correspond closely to those required by the formula of autunite, after combining the sodium and calcium.

The  $\omega$  index<sup>5</sup> of this preparation is about 1.605, and  $\epsilon$  is not much lower, the birefringence being moderate. Most of the plates, averaging from about 0.01 to 0.05 mm. in width (and very much thinner) are isotropic on basal sections and uniaxial negative.

As the first object in this preparation of artificial autunites, was to make the calcium compound corresponding to the natural mineral, the unexpected result of obtaining sodium as an essential constituent was obviated, though still retaining a concentrated solution of a brine as "salting out" medium, by substituting calcium chloride (of a density of 1.25 or higher) for sodium chloride. The precipitation was repeated with the same proportion of calcium phosphate and uranium nitrate, and a similar well crystalized product was obtained. The well washed product, after being air dried for several days, gave the following results:

##### ANALYSIS OF THE CRYSTALS FROM CaCl<sub>2</sub> BRINE.

	Per cent	Ratios
P <sub>2</sub> O <sub>5</sub>	15.95	.112 or 1
UO <sub>3</sub>	63.00	.220 or 2
CaO	7.17	.128 or 1
H <sub>2</sub> O (ign.)	13.84	.769 or 6.7
	99.96	

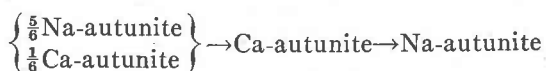
<sup>4</sup> Hillebrand, W. F., Carnotite and tyuyamunite and their ores in Colorado and Utah. *Amer. Jour. Science*, vol. 8, pp. 201-216, 1924, especially pp. 214-216; also earlier, same Journal, vol. 7, p. 439, 1913.

<sup>5</sup> All the optical determinations were made by W. T. Schaller.

The composition is the same as that of natural autunite, the ratios yielding the formula  $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . Optically, the material was very similar to natural autunite. The 4 and 8 sided plates were either isotropic or weakly birefracting with a characteristic gray-blue birefringent color. Twinning lamellae parallel to (100) are abundant.  $\omega$  is about 1.600 and  $\epsilon$  about 1.590, both being slightly variable. Another calcium product, obtained later by a similar process, gave uniaxial plates, containing 15.42 per cent  $\text{H}_2\text{O}$ , with  $\omega = 1.598$  and  $\epsilon$  about 1.586 and still a third similar product has the same  $\omega$  value.

A sample of this artificial calcium autunite was then digested with a solution of sodium chloride (about half saturated) on the steam bath for at least 2 days when the resultant product was found to be free from calcium and to contain much sodium. This product, with 16.09 per cent  $\text{H}_2\text{O}$ , consisted of uniaxial plates with  $\omega = 1.583$  and  $\epsilon = 1.566$ . Similarly, by starting out with a pure sodium compound and digesting it with a strong solution of calcium chloride, the sodium was replaced and the calcium compound again obtained.

As apparently the sodium and the calcium can replace each other with great ease, it seemed desirable to make a preparation of the sodium-autunite entirely free from calcium. As considerable material of the first made product—the 5/6 sodium, 1/6 calcium, with 5.62 per cent  $\text{Na}_2\text{O}$  and 1.10 per cent  $\text{CaO}$ —was available, a sample of it was first changed to the pure calcium-autunite. This was not analyzed quantitatively but only tested qualitatively. The isotropic plates had an  $\omega$  index of 1.601 and  $\epsilon$  index of  $1.588 \pm$ . This change to a calcium-autunite was made in order to verify the suspicion that sodium and calcium can replace each other in these compounds with great ease in either direction, the character of the brine used being the factor determining the composition of the product. A simpler method for the preparation of the pure sodium-autunite would have been to treat again the original product with a second  $\text{NaCl}$  brine. The calcium product obtained was then digested with  $\text{NaCl}$  brine and the calcium replaced by sodium. The sequence of formation of these three autunites can be expressed as follows:



Analysis of this end product, given below, showed that it represents the pure sodium-autunite, with the formula  $\text{Na}_2\text{O} \cdot 2\text{UO}_3 \cdot n\text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . In size, the plates average from about 0.05 to 0.10 m.m. across.

## ANALYSIS OF SODIUM-AUTUNITE.

	Per cent	Ratios
$\text{P}_2\text{O}_5$	16.00	.113 or 1
$\text{UO}_3$	64.51 by diff.	.224 or 2
CaO	None	.....
$\text{Na}_2\text{O}$	6.23	.101 or 1
$\text{H}_2\text{O}$ (ign.)	13.26	.737 or 6.5
	<hr/> 100.00	

Examined optically, most of the plates show a very slight birefringence.  $\omega = 1.582$  and  $\epsilon = 1.562$ .

One of the sodium-autunites prepared gave an anomalous result, in that while free from calcium, it contained an insufficient amount of sodium. There was no reason for suspecting such an anomalous result during its preparation. The 5/6 calcium, 1/6 sodium-autunite was used as a starting point. This was changed to the calcium-autunite which was then treated with a NaCl brine to change it to the sodium compound. The analysis showed a lower sodium content than previously obtained but also a higher water content.

## ANALYSIS OF ANOMALOUS SODIUM-AUTUNITE.

	Per cent	Ratios
$\text{P}_2\text{O}_5$	16.30	.115 or 1
$\text{UO}_3$	64.20	.223 or 2
CaO	None	<hr/>
$\text{Na}_2\text{O}$	3.96	.064 or 0.57
$\text{H}_2\text{O}$ (ign.)	15.88	.882 or 7.81
	<hr/> 100.34	

Optically, this sample did not differ from the sodium-autunite previously described except that many of the larger plates had an  $\omega$  index slightly higher than 1.580 and some of the smaller plates had an  $\omega$  index slightly under 1.580. The variation however was not greater than was observed in many of these preparations and it could not be definitely said that the preparation consisted of two

distinct compounds. There is a close approximation, in the ratios, to a compound of the type  $\frac{1}{2}\text{Na}_2\text{O}\cdot 2\text{UO}_3\cdot \text{P}_2\text{O}_5\cdot 8\text{H}_2\text{O}$ , which is suggestive of the fact that Na and not  $\text{Na}_2$  replaces Ca. On the other hand, the water content being higher than in the sodium-autunite previously described, the preparation may be: (1) either a mixture of  $\text{Na}_2\text{O}\cdot 2\text{UO}_3\cdot \text{P}_2\text{O}_5\cdot n\text{H}_2\text{O}$  with  $\text{H}_2\text{O}\cdot 2\text{UO}_3\cdot \text{P}_2\text{O}_5\cdot n\text{H}_2\text{O}$ , or (2) some water may function as  $\text{Na}_2\text{O}$  (or hydrogen as sodium), its formula can be written  $(\text{Na},\text{H})_2\cdot 2\text{UO}_3\cdot \text{P}_2\text{O}_5\cdot n\text{H}_2\text{O}$ . The previously described sodium-autunite with 6.23 per cent  $\text{Na}_2\text{O}$ , however, shows clearly the existence<sup>6</sup> of a compound with the formula  $\text{Na}_2\text{O}\cdot 2\text{UO}_3\cdot \text{P}_2\text{O}_5\cdot n\text{H}_2\text{O}$ .

The ease of base replacement so far encountered suggested that other bases might just as readily replace the sodium or the calcium. As a quantity of the sodium-autunite, containing 6.23 per cent  $\text{Na}_2\text{O}$  and corresponding to the formula  $\text{Na}_2\text{O}\cdot 2\text{UO}_3\cdot \text{P}_2\text{O}_5\cdot n\text{H}_2\text{O}$ , was available this compound was used as a starting point for the preparation of the subsequent base-replacements. Using a solution of the chlorides of potassium, barium, manganese, copper, nickel, cobalt, and magnesium, the respective base replacement was easily effected and corresponding autunites prepared. Only lead was unsuccessful as a base replacement.

*Potassium.* By digesting the sodium autunite with a brine of KCl for several days, the crystals showed, by flame test, the presence of considerable potassium with only a negligible quantity of sodium. These crystals were not analyzed. The plates were 8-sided, and somewhat larger than usual with an average width of about 0.2 mm. Many of the larger plates are not rectangular in outline but have an angle of about  $82^\circ$  instead of  $90^\circ$  and seem to have been

<sup>6</sup> The composition of the anomalous sodium-autunite raises the question as to the replaceability of sodium and calcium. The preparation of the compound  $\text{Na}_2\text{O}\cdot 2\text{UO}_3\cdot \text{P}_2\text{O}_5\cdot n\text{H}_2\text{O}$ , with 6.23 per cent  $\text{Na}_2\text{O}$ , shows that  $\text{Na}_2\text{O}$  can replace CaO, but the formation of the so-called anomalous sodium-autunite with only 3.96 per cent  $\text{Na}_2\text{O}$ , brings to attention the question as to whether or not one Na replaces one Ca, or expressed as oxides, one  $\text{Na}_2\text{O}$  may replace  $2\text{CaO}$ . Prof. Winchell has offered to undertake an X-ray investigation of these compounds and it is hoped that such a study may reveal relations that are pertinent to the question. The varying hydration is a factor that must be considered as the quantity of water held by the material is directly a function of the hygroscopicity of the surrounding air as well as a function of temperature. It is not practicable to continue the investigation in this laboratory and the problem is left open for anyone desirous of undertaking it.

changed to a modification that is not tetragonal, possibly related to bassetite. The plates show a fine rectangular grating structure, resembling microcline, and most of them give a negative uniaxial figure though some are biaxial with a variable but small axial angle.  $\omega$  is about 1.575 and  $\epsilon$  about 1.553.

*Barium.* Using a barium chloride brine, the resultant product contained 15.3 per cent BaO and 11.0 per cent H<sub>2</sub>O. The ratio of H<sub>2</sub>O to BaO is 6.1 to 1.0. These values for BaO and H<sub>2</sub>O are like those of the natural mineral uranocircite. Optically most of the plates are uniaxial, the basal plates showing many broad polysynthetic twinning lamellae after both (100) and (110).  $\omega$  is about 1.613 and  $\epsilon$  about 1.604.

*Manganese.* A manganese brine yielded a product which contained about 8 per cent MnO and 15 per cent H<sub>2</sub>O. Ratio of H<sub>2</sub>O to MnO = 7.6. Optically the plates show all the varieties described in the introduction. Most of the plates are broken up into a mosaic of irregular areas, some isotropic and others weakly birefracting. Some plates are biaxial with a moderately high birefringence. Some show the abnormal blue interference color. Diagonal twinning lamellae (after  $m(110)$ ) are abundant.  $\omega$  is about 1.60, varying from 1.598 to 1.601.

*Copper.* Treatment with copper chloride showed that copper readily enters into the mineral, the resultant product being decidedly greenish but complete replacement was not obtained, judging by the color and qualitative tests. As the copper compound is well known as a mineral, the experiment was repeated and the product partially analyzed. Its color was of a much deeper green color than the first product and evidently showed a greater replacement. The copper, nickel, and cobalt compounds were obtained by an overnight treatment on the steam bath in a covered beaker with the appropriate brine. As a result of the many experiments made, it seems desirable to let the product react with the brine for 2 or 3 days, in order to obtain complete replacement.

The copper compound, with  $\omega = 1.608$  on the average, but slightly variable, gave on analysis:

PARTIAL ANALYSIS OF COPPER-AUTUNITE.

	Per cent	Ratios
CuO	5.61	.070
Na <sub>2</sub> O	0.73	.012
H <sub>2</sub> O	15.62	.868 or 10.6



*Nickel and cobalt.* These two bases also readily replace the sodium at least to a considerable degree. The nickel product was of a greenish-yellow color and the cobalt of a pinkish brown.

*Lead.* Judging by the fact that lead functions as sodium in the minerals of the jarosite group, attempts were made to prepare a lead autunite by similar treatment of the sodium autunite with a lead brine. The resultant product was not homogeneous nor well crystallized and the lead content was 9 per cent above the theoretical value. However, a lead autunite was prepared by the method of slow precipitation and crystallization from a dilute solution. A solution of the mixed nitrates of uranium, calcium and lead was allowed to react slowly through a volume of 4 liters of water with a weak solution of phosphoric acid, (0.01 molar) which was more than enough to precipitate the bases.

All the salts were present in proper proportion to form calcium or lead autunite, with a 1:1 molecular ratio between the calcium and the lead. This arrangement was intended to permit a natural selection of base with respect to the calcium or the lead. After about two weeks the crystals obtained were washed free from soluble salts and analyzed for calcium and lead. Found, PbO, 19.5 per cent; CaO, none; H<sub>2</sub>O, 13.1; theory for lead, 20.6. Ratio of H<sub>2</sub>O to PbO = 8.4. The optical examination showed that much of the material was matted together into compact flakes of irregular shape, with some square plates. Many of the plates were slightly birefringent and biaxial. The material did not look as uniform or as perfect as the other preparations, or at least the individual crystals were not so perfect nor so freely developed. The  $\omega$  index is about 1.625.

Some of this lead-autunite was recrystallized by dissolving in a little HNO<sub>3</sub> and then neutralizing with CaCO<sub>3</sub> and letting the product slowly crystallize out after dilution to six liters. This product came out in well formed 8-sided plates, very weakly birefracting on the base and with an  $\omega$  index of 1.627.

*Magnesium.* Treatment with a magnesium chloride brine gave a product containing: MgO, 4.36 per cent; Na<sub>2</sub>O, trace; H<sub>2</sub>O, 15.74 per cent. Ratio of MgO:H<sub>2</sub>O = 8.1. The material is lighter colored than any of the other preparations. Optically the plates are either isotropic or weakly-birefracting on the base. The  $\omega$  index is variable, with a mean value of about 1.58.

## SUMMARY

Artificial autunites were made by slow crystallization from dilute solutions and by a "salting out" process, using a chloride as the precipitating agent. Starting with sodium-autunite, and to a lesser degree with calcium-autunite, a series of base exchange autunites were prepared by treating the sodium-autunite with a strong solution of the chloride of the element which it was desired should replace the sodium. In this way, calcium, potassium, barium, manganese, copper, nickel, cobalt, lead, and magnesium autunites were easily prepared. Treating the sodium-autunite with a  $\text{CaCl}_2$  brine readily changed it to a calcium-autunite and treating the calcium-autunite with a  $\text{NaCl}$  brine readily changed it to the sodium-autunite. Apparently this change can be repeated alternately as often as desired.

Most of these autunites so prepared contain less than 8 molecules of water. Their refractive indices are summarized in the following table, the values being expressed as  $\omega$  and  $\epsilon$ , even though some of the products are biaxial and have the indices  $\gamma$ ,  $\beta$ , and  $\alpha$ . For these biaxial modifications,  $\gamma$  is represented by  $\omega$  and  $\beta$  is very close to  $\gamma(\omega)$ . The quantity of water present changes the indices appreciably, but no attempts were made to correlate the hydration of the substances with the humidity of the air, or to closely connect the indices with their water content.

REFRACTIVE INDICES OF VARIOUS ARTIFICIAL AUTUNITES.

Composition of exchangeable base	$\frac{1}{2}\text{Na}$ , $\frac{1}{6}\text{Ca}$	Ca	Na	Anomalous Na	K	Ba	Mn	Cu	Pb	Mg
Ratio of $\text{H}_2\text{O}$ to exchangeable base	6.5	6.7	6.5	7.8	—	6.1	7.6	10.6	8.4	8.1
$\omega$	1.605	1.600	1.582	1.580	1.575	1.613	1.60	1.608	1.625	1.58
$\epsilon$	—	1.590	1.562	—	1.553	1.604	—	—	—	—

As already stated in a footnote, the investigation can not be carried any further in this laboratory and the entire problem is open to anyone interested. In addition to the problem of base-replacement, there is the similar one of acid-replacement, for the  $\text{P}_2\text{O}_5$  can probably be replaced with  $\text{As}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ , etc., with similar relative ease.

The ease of such base-replacement is a confirmation of earlier

work along similar lines, some of which was done many years ago. For example, Clarke and Steiger noted<sup>7</sup> the "easy replaceability of the soda in analcite" by ammonia and by silver oxide. Incidentally such equivalent functioning of  $\text{Na}_2\text{O}$ ,  $(\text{NH}_4)_2\text{O}$ , and  $\text{Ag}_2\text{O}$ , has been strikingly verified mineralogically by the later discovery of the minerals natrojarosite, ammoniojarosite, and argentojarosite.

<sup>7</sup> Clarke, F. W., and Steiger, George. The action of ammonium chloride upon silicates, *U. S. Geol. Survey Bull.* No. 207, 1902.