

cept those of kleinite, on which we have not seen it. It is usually present as globular irregular masses associated directly with the other minerals. Globules often project from small cavities on the surfaces of crystals of terlinguaite, eglestonite and montroydite, and are sometimes to be seen in the interior of crystals of terlinguaite and montroydite, notably the latter. While much of it is in the form of a fairly pure liquid, a good deal is mixed with powdery oxychlorides as a sort of stiff paste having a gray or greenish color and irregularly associated with the plainly crystallized oxychlorides and montroydite. The proximate determination of this gray or greenish mass is almost impossible. Some of the mass has a yellowish, almost metallic sheen, which is perhaps largely an iridescent effect.

Summary.

Kleinite, as announced in 1905, belongs to the so-called mercury ammonium compounds, but no probable formula can be deduced from the analyses. It may be a mixture of a mercury-ammonium chloride in great preponderance, $\text{NHg}_2\text{Cl} \cdot 1\frac{1}{3}\text{H}_2\text{O}$, with an oxychloride and sulphate or oxysulphate of mercury.

Terlinguaite is a mercuric-mercurous oxychloride, $\text{HgO} \cdot \text{HgCl}$, the formula of Moses being confirmed and the mixed nature ascertained by tests.

Eglestonite is a mercurous oxychloride, $\text{Hg}_2\text{O} \cdot 2\text{HgCl}$, the first authentic instance of such a compound, either artificial or native, and not $\text{Hg}_6\text{Cl}_3\text{O}_2$, as believed by Moses.

Montroydite is mercuric oxide, as supposed by Moses, and proven now by direct determination of its oxygen content.

LABORATORY U. S. GEOLOGICAL SURVEY,
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SOME NEW DOUBLE PHOSPHATES OF CHROMIUM.¹

BY LOUIS J. COHEN.

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In attempting to prepare a double phosphate of chromium under the conditions of acidity already described in the formation of the iron and aluminum salts,² negative results were obtained; no precipitate was formed even when an extremely large excess of diammonium phosphate was added. When, however, the acidity was diminished, a precipitate was readily obtained.

The chromium solution employed was prepared by treating a little more than twenty grams of Kalilbaum's chromium hydroxide with 45.2

¹ Read at the April meeting of the N. Y. Section of the Amer. Chem. Society.

² This Journal 29, 5.

cc. of hydrochloric acid (1.2)¹. After slightly warming, the volume was made up to 500 cc., thoroughly mixed, allowed to stand and finally filtered from the undissolved hydroxide. The resulting clear solution was acid to litmus and contained approximately six grams of chromium chloride in 100 cc.

As it was impossible to previously determine the acidity required to form a double phosphate, four precipitations were made yielding respectively the products "A," "B," "C," and "D," referred to below, from solutions containing varying amounts of hydrochloric acid; the total volume in each case being 400 cc.

As the method of preparation was the same for all, a detailed description of one will suffice.

Sample A. A solution consisting of 100 cc. of the chromium chloride solution, 90 cc. of water and 10 cc., of hydrochloric acid (1.2), was heated to 80°. To this was gradually added, with constant stirring, 50 grams of diammonium phosphate dissolved in 200 cc. of water. The green precipitate which first formed was gelatinous in character, but on heating on an asbestos pad, for one-half hour, was observed to change at 90° to a dense and granular form, which rapidly settled, leaving a clear, slightly green supernatant-liquid. After digestion on a boiling water-bath for one-half hour the clear liquid was siphoned off and the residual compact mass washed by decantation with alcohol (1:1), containing 0.1 per cent. of ammonium chloride; and finally washed on a filter with alcohol (1:1) till free of chlorides; it was then dried in the water oven and analyzed. The supernatant liquid was acid to litmus, and gave a strong test for phosphoric acid and ammonia; showing that an excess of the precipitant had been added.

Sample B was prepared under the same conditions, except as regards acidity; which in this case was 15 cc.; in sample C, 1 cc. was used; with sample D no acid was added.

The filtrates from each of the last precipitates were slightly green, acid to litmus, and gave strong tests for phosphorus and ammonia, showing that an excess of the precipitant had been added.

There appeared to be scarcely any difference in the color of samples A, B and C, which were all light green.

Sample D possessed a bluish-slate color when first formed, which on continued heating acquired a violet tinge and finally on drying in the water oven became dark green.

Method of Analysis.—In the analysis of the chromium compounds, considerable difficulty was encountered in the determination of phos-

¹ This being the calculated amount of hydrochloric acid for the complete solution of 20 g. of the hydroxide.

phorus. The usual method of separation with ammonium molybdate in a nitric acid solution, was incomplete; the ammonium phosphomolybdate invariably carrying down with it appreciable amounts of chromium, as was shown by its olive color. Precipitating in a larger bulk, followed by thorough washing with dilute nitric acid solution having failed to remove the contamination, reprecipitation was resorted to. This gave a more yellow precipitate, but this still retained chromium, as shown by the purple tint of its solution in ammonia, and by the slight color of the magnesium pyrophosphate obtained therefrom. Precipitation of the phosphorus with barium chloride in an alkaline solution, was next tried; but this method also failed to give a satisfactory separation. These methods were, therefore, abandoned, and those based on the preliminary oxidation of the chromium tried; after some experimentation the following method was adopted.

About one gram of the sample was treated in a beaker with a solution of sodium hydroxide (prepared from sodium) and warmed till complete solution took place. Sodium peroxide was then added in small amounts and the solution brought rapidly to a boil. After a clear yellow solution had been obtained, the boiling was continued for fifteen minutes, the solution was cooled, neutralized with sulphuric acid, transferred to a 500 cc. flask, and diluted to the mark. 50 cc. were pipetted out, diluted to 150 cc., and then made slightly alkaline with ammonia. The phosphorus was precipitated with magnesia mixture in the usual way and weighed as pyrophosphate. In the filtrate or in another 50 cc. the chromium was determined volumetrically by titrating with standard thiosulphate solution the iodine liberated. The ammonia was determined in the usual way.

On the assumption that the compound contained three molecules of water at the temperature of drying the analytical results were :

	Found Per cent.	Theory for (NH ₄) ₂ HPO ₄ · 2 Cr PO ₄ · 3H ₂ O Per cent.
P	19.63	19.36
Cr	21.43	21.69
NH ₄	7.55	7.52

The close agreement sufficiently warrants the supposition that at the temperature of drying, the salt retains three molecules of water, and has the composition represented by the formula.

Analysis of samples C and D gave results leading to the formula
5 NH₄H₂PO₄ · 2 Cr PO₄ · 4 Cr (OH)₃.

	Found D Per cent.	Theory for 5NH ₄ H ₂ PO ₄ · 2 Cr PO ₄ · 4 Cr (OH) ₃ Per cent.
P	17.21	16.93
Cr	24.43	24.38
NH ₄	7.06	7.04

The reduction of the acidity therefore results in the formation of a

basic double phosphate. On ignition all the samples decompose giving off water and ammonia. The double chromium phosphates differ from those of aluminum and iron in their non-formation from strongly acid solutions, their greater tendency to form basic salts and their ability to combine with the secondary ammonium phosphate.

The Double Phosphate of Chromium and Sodium.— $\text{Na}_2\text{HPO}_4 \cdot 2\text{CrPO}_4$. From the results of experiments with diammonium phosphate upon hydrochloric acid solutions of the chlorides of iron, aluminum and chromium, it seemed quite probable that corresponding sodium and potassium salts could be prepared by substituting the disodium and dipotassium phosphates respectively for the diammonium salt. In the case of the double chromium phosphate, however, this supposition appeared to be contradicted by the work of the Bloxam¹, who, on boiling an acetic acid solution of a chromium salt with disodium phosphate, obtained a green precipitate which from the results of his analysis, he regards as a basic chromium phosphate retaining five molecules of water at 100° . He states that his product contained admixed impurities, but no mention is made of the nature and extent of the latter in the analytical results. The readiness with which these double phosphates hydrolyze when excessively washed with water, and it appears that Bloxam's product was so treated, and the fact that no mention is made of the absence of sodium in his product, seem to show that he first obtained a double phosphate of sodium and chromium which on prolonged washing with water changed to the basic compound he finally obtained and analyzed. This supposition is strengthened by the work of Steinschneider², who found that on excessive washing, with water his double phosphate of sodium and copper was converted to a basic phosphate, which was free from sodium.

Preparation.—To 40 cc. of the chromium chloride solution used in the previous preparations, diluted to 100 cc., sodium hydroxide was added until a slight but permanent precipitate formed; after clearing with a drop or two of acetic acid, 20 cc. more of 50 per cent. acetic acid was added and the resulting solution heated on an asbestos pad; 50 grams of disodium phosphate dissolved in 200 cc. of water were then gradually added with constant stirring and the volume made up to 400 cc. The resulting clear solution was then heated; no precipitate formed at first, but on continued heating a cloudiness soon formed followed by the formation of a green gelatinous precipitate which on further heating to 100° became dense; it was then transferred to a boiling water-bath for a half hour and allowed to stand over night. The next day the clear, colorless, supernatant liquid was siphoned off; it was found to be acid

¹ Chem. News, 52, 194-195.

² Uber die phosphates des Kupfers, Dr's Dissertation, p. 35.

and gave a strong test for PO_4 . The precipitate was washed twice by decantation with alcohol (1:1) then transferred to a filter and washed again with alcohol (1:1) till free of chloride; it was then dried in a water oven and analyzed.

The dried precipitate possessed a green color, considerably lighter than that of any of the chromium compounds already mentioned.

Analysis gave:

	Found Per cent.	Calculated for $\text{Na}_2\text{HPO}_4 \cdot 2\text{CrPO}_4 \cdot 5\text{H}_2\text{O}$ Per cent.
Cr.....	19.45	19.77
P	17.56	17.68
Na	8.79	8.75

These results fully confirm the supposition to which the results of Bloxam's basic chromium phosphate lead, *viz.*, that the addition of disodium phosphate to a solution of chromium chloride precipitates a double phosphate of chromium and sodium, which readily hydrolyzes on excessive washing with water to a basic phosphate.

In conclusion I wish to acknowledge my indebtedness to the late Prof. E. H. Miller for suggestions in the early stage of this work and also to express my thanks to Prof. H. C. Sherman, Prof. J. L. R. Morgan and Dr. F. Metzger for valuable assistance.

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THE ANNEALING OF STERLING SILVER.

BY WM. H. WALKER.

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It was early found by the workers in metallic silver that the ware made from an alloy of copper and silver was superior in almost every respect to that made from pure silver. Although quite a wide variation in the relative amounts of these two metals can exist and still produce a usable alloy, that proportion which has been accepted as a standard and which is called "Sterling" is composed of 7.5 per cent. copper and 92.5 per cent. silver. As is the case with other alloys, Sterling silver suffers a change in its physical properties when subjected to mechanical treatment such as rolling, drawing, stamping, etc., becoming hard, stiff and brittle. When the alloy is annealed by heating it to low redness, these undesirable properties doubtless due to molecular strains, disappear, and the ware may be subjected to further mechanical treatment. These frequent heatings produce on the alloy a scale of black copper oxide which so long as the articles were finished by hand was entirely removed by the subsequent filing and buffing necessary to produce the required polished surface. When the more modern methods of rolling and stamp-