

ART. XXIV.—*On Tychite, a New Mineral from Borax Lake, California, and on its Artificial Production and its Relations to Northupite*; by S. L. PENFIELD and G. S. JAMIESON.

Historical.—The new mineral to be described in this paper was discovered by the merest chance in 1895, when some minerals from Borax Lake, San Bernardino County, California, were being studied by one of the present writers (Penfield). At the time mentioned, word had been received from Mr. Warren M. Foote of Philadelphia that he had some unknown minerals from the Borax Lake region, and arrangement was made for their examination in the mineralogical laboratory of the Sheffield Scientific School. One of the minerals, which proved to be a new species, consisted of octahedral crystals, averaging about 3^{mm} in diameter, and concerning it Mr. Foote wrote that it was a carbonate of magnesium and sodium containing chlorine. The material sent for examination consisted of a large number of the octahedral crystals, and from amongst them a small one, which was perfect in form and seemed to be in every way typical of the lot, was selected for the purpose of making a few preliminary tests. It was brought in contact with a drop of nitric acid on a watch glass and dissolved with effervescence; the solution gave the flame test for sodium, a minute drop of it gave the reaction for magnesium with ammonia and sodium phosphate, but a test for chlorine with silver nitrate gave a negative result. Thinking over what else might possibly be present, the idea of a sulphate suggested itself, and a test with barium chloride indicated the presence of the SO_4 radical. Accordingly, a letter was sent to Mr. Foote informing him that there evidently was some mistake, for the mineral he had sent proved to be a sulphate and not a chloride. This elicited an immediate reply from Mr. Foote, stating that, on the contrary, the mistake was on our part, for he had always obtained the test for chlorine and had repeated the experiment with like results; thereupon the test was repeated by us, and the presence of chlorine was found in one crystal after another. The fact, therefore, was established, that in the material sent there were two minerals crystallizing in octahedrons, one containing the sulphate radical, the other chlorine, and that by chance a crystal of the rarer sulphate happened to be the one first selected for making the initial examination. A preliminary notice of the chlorine compound was published by Mr. Foote,* who named the mineral *northupite* after Mr. C. H. Northup of San Jose, California,

* This Journal (3), 1, p. 480, 1895.

who first observed the new mineral and supplied the material for investigation. A complete study of the chemical composition and physical properties of the new compound was subsequently made by Pratt, who found the composition to be $MgCO_3$, Na_2CO_3 , $NaCl$, his results being published in this Journal.*

Being assured of the existence of a second, new, octahedral mineral, associated with the northupite, Mr. Foote generously responded to our request to send to New Haven his entire stock of crystals in order that a search might be made for the missing sulphate. The following simple method of testing was employed, which did not in any way injure the specimens: Some dilute nitric acid containing a little silver nitrate was prepared, and with a broom-straw a minute drop of the liquid was applied to each crystal. Thus, if chlorine was present, a little silver chloride would be formed and the drop of liquid would become milky-white. In testing several hundred crystals in this way, only two were found which did not give the reaction for chlorine. One of these was a small but perfect octahedron, the other a small cluster of octahedrons, of somewhat inferior quality: together they weighed only about 0.10 gram. It was hoped, however, that by sacrificing the specimens for chemical analysis sufficient determinations could be obtained for deriving the formula; but in this we were disappointed, for, unfortunately, the analysis met with an accident before a single determination had been made. We were thus compelled to abandon the hope of determining the composition of the new mineral until other crystals should be found in new lots of the northupite.

Recently our attention was called to the unknown sulphate by observing in the stock of Mr. Lazard Cahn of New York a supply of northupite crystals which he generously loaned to us for examination, but when tested they all proved to be the chlorine compound. Likewise Mr. Warren M. Foote of Philadelphia has been kind enough to send us his entire stock of northupite, consisting of something over four thousand crystals, among which we had the good fortune of finding one small octahedron, weighing but 0.0109 gram. Curiously enough, this was among the last ten crystals which were tested, and was found after hope of obtaining the desired sulphate had practically been given up.

Artificial production.—Believing that the unknown sulphate would prove to be closely related to northupite, and knowing that de Schulten† had succeeded in making the latter artificially, it occurred to us that possibly the wished for sulphate

* This Journal (4), ii, p. 133, 1896; also, iii, p. 75, 1897.

† Bull. Soc. Franc. de Min., vol. xix, p. 164, 1896.

might also be prepared synthetically. Following in general the method of de Schulten, 8 grams of Na_2CO_3 and 34 grams of Na_2SO_4 were dissolved in 120^{cc} of water, and to the solution 1.4 grams of MgSO_4 were added, which immediately produced an amorphoid precipitate, presumably of some basic magnesium carbonate. The mixture, contained in a flask, loosely stoppered to prevent evaporation, was then heated on a steam bath. By using chlorides in the place of sulphates, as described above, de Schulten succeeded in making northupite in a crystallized condition in about seven hours; in our experiment, however, we waited five days, the solution being heated without interruption, before any signs of crystallization appeared. In the meantime we had tried heating a similar mixture in a sealed tube at a high temperature, without definite results, and had practically given up hope of obtaining the desired crystals. It was almost a matter of accident, therefore, that the flask containing the mixture was left standing on the steam bath for so long a time. When the crystallization had once started, however, it apparently proceeded quite rapidly, and the insoluble material in the flask was almost wholly converted into octahedral crystals, very symmetrical in development and remarkably uniform in size, about 0.15^{mm} in diameter. Having once produced a crop of crystals, we are now able, by "seeding" or adding some of the product already formed to a new experiment, to produce crystals in fifteen hours, though it still seems to take several days to complete the reaction. When examined under the microscope, it was found that each crystal contained minute inclusions, presumably of basic magnesium carbonate, but the inclusions constituted a very small proportion of the total bulk of the material. The crystals were next suspended in acetylene tetrabromide, diluted with benzol, and it was found that they all floated when the specific gravity was 2.594, and on diluting to 2.583 almost all of the material sank. The mean of the two values, 2.588, may therefore be taken as the specific gravity of the mineral. It was found that the lighter crystals, left floating on the heavy solution, were perceptibly richer in inclusions than those which sank at 2.583. The crystals are quite hard and give a gritty sensation when ground in an agate mortar. They scratch calcite and probably, like northupite, have a hardness between 3.5 and 4. The crystals are isotropic when examined in polarized light. Using two surfaces which come together at the apex of an octahedron as a prism, it was possible to determine approximately the index of refraction, but the surfaces of the crystal were not good enough to make the determination accurate beyond the second place of decimals: the value found was 1.510, while n_y for northupite was 1.514.

An analysis of the purest material, separated by means of the heavy solution, gives the formula $2\text{MgCO}_3 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$, the results being as follows :

	I.	II.	Theory.
SO ₃	15·08	15·06	15·33
CO ₂	33·55	33·45	33·72
MgO.....	15·83	15·77	15·33
Na ₂ O.....	35·49	35·65	35·62
	<hr/>	<hr/>	<hr/>
	99·95	99·93	100·00

The slight discrepancies between the results of the analyses and the theory are probably to be accounted for by the presence in all of the crystals of the minute inclusions mentioned on the previous page.

The finely powdered salt does not dissolve to any extent in hot water, nor does it suffer decomposition. Some powder, boiled with water for a considerable time, then filtered and dried, gave the following results:—SO₃, found 15·21 per cent, theory 15·33 per cent. The filtrate gave only a slight reaction of a sulphate when tested with barium chloride.

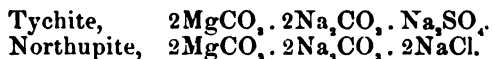
Name.—We have named the new and rare sulphate *tychite*, from τυχή, meaning luck or chance, a name which it well deserves, when it is considered that out of fully five thousand specimens examined, the very first crystal and one of the ten last crystals tested proved to be the sulphate, and only two other specimens were found, the ones lost in an unsuccessful attempt to make an analysis.

Comparison of the artificial salt with the natural mineral.—Without question, the artificial salt is identical with the mineral found at Borax Lake: they both contain the same constituents. They crystallize not only in the same system, but also in octahedrons. They are isotropic, although the last crystal of tychite found showed some slight action on polarized light, which seemed to be confined only to the exterior portions of the crystal, for fragments from the interior were wholly isotropic. The specific gravity of the artificial salt is 2·588, of the crystal examined by Pratt (the analysis of which was lost) 2·456, and of the last crystal found by us 2·30. The last crystal, however, contains numerous inclusions, which undoubtedly account for its low specific gravity. As far as can be recollected, the crystal examined by Pratt was very white and pure, but not equal in transparency to the artificial crystals. Both Pratt's determination, 2·456, and ours of the artificial salt, 2·588, are somewhat higher than the specific gravity of northupite, as might be expected from differences in composition: Pratt found the specific gravity of northupite to be

2380, and de Schulten determined that of the artificial salt as 2377. By using two of the faces which meet at the apex of the octahedron as a prism, we have succeeded in determining the index of refraction of the last crystal found. The surfaces of the octahedron were not very perfect, and had to be covered over for the most part, taking the reflections of the signal from only the tip end of the crystal, and the refraction of light through the same. The value obtained, $n_v=1.508$, compares favorably with that of the artificial salt, 1.510, especially when it is taken into consideration that the condition did not favor exact determinations in either case. A further argument for the identity of tychite and the artificial salt, if any is needed, is that at Borax Lake both tychite and northupite occur together, and were formed undoubtedly under similar conditions, while in the laboratory either of these closely related chemical compounds may be made by only varying the conditions of the experiment by using sodium sulphate for the one and sodium chloride for the other.

Of the four specimens of tychite thus far found, three have been very symmetrically developed octahedrons, but small, measuring not over 3^{mm} in diameter, and noticeably whiter than the average of the northupites. It is the small size of the crystals which favored the discovery of the new mineral, for in the original preliminary test one of the smallest and whitest specimens was selected, both because of its evident purity, and also with the idea of not using up any more material than was necessary. Those who may happen to have northupite crystals and wish to search for specimens of the new mineral, may look for tychite therefore among the smaller crystals. We are informed in a recent letter from Mr. Northup that the chances of finding additional crystals of tychite, or of the associated minerals, northupite and pirssonite, are too remote to be seriously considered, as the old borax works are now dismantled. Tychite, therefore, promises to be a very rare mineral, unless a new locality for it happens to be discovered. The single crystal which we recently had the good fortune to find, Mr. Foote has generously presented to the Brush Collection of the Sheffield Scientific School, and both for this gift and for the interest he has taken in assisting us in our investigation we take pleasure in expressing our most sincere thanks.

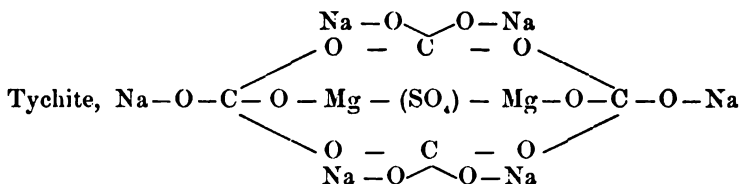
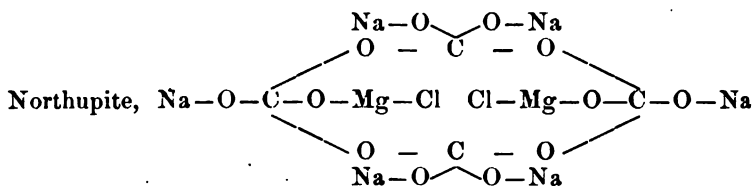
Comparison of tychite and northupite.—The two minerals, found so intimately associated with one another and both crystallizing in octahedrons, are chemically closely related, but in order to show the relation it is necessary to double the formula of northupite, as determined by Pratt. The compositions may then be expressed as follows :



Other physical properties are given below:

	Specific gravity.	Index of refraction, n_D .
Tychite,	2.456 natural.	1.508 natural.
	2.588 artificial.	1.510 artificial.
Northupite,	2.380 natural.	1.514 natural.
	2.377 artificial.	

Theoretical.—There seems to be far more interest connected with the present investigation than the mere description of a new species. Although northupite is somewhat slowly soluble in cold water, and is quickly decomposed by boiling water with the separation of magnesium carbonate, tychite is almost insoluble, even when its fine powder is treated with boiling water. Unlike most insoluble substances, however, which precipitate quickly as soon as the constituents necessary for their formation are brought together, northupite and tychite are formed slowly. In de Schulten's experiment, northupite was obtained after seven hours heating, and in ours it took nearly as many days of continued heating to obtain crystals of tychite. It would seem as though the slowness with which these substances are formed might be taken as an indication of their having a complex molecular structure, and that the element of time is necessary for the arrangement of the atoms in a state of equilibrium. Just what the arrangement of the atoms is, we are not able to determine, but the simplest and most symmetrically developed formulas which suggest themselves are the following:



In these formulas the four carbon atoms are united by oxygen in ring formation, which it may be assumed it takes some time to establish, but, when once established, accounts

for the stability of the compounds. It is possible also that the assumed symmetrical arrangement of the atoms in the molecule is the cause of the crystallization of these compounds in the isometric system, for, as a rule, salts of a highly complex nature crystallize in some system other than the isometric. Moreover, if the above formulas are correct, it might be expected that tychite would be more difficultly soluble in water than northupite, for the SO_4 radical uniting the two magnesium atoms would serve, as we might say, to protect the latter from attack, while the sodium atoms could not be taken away without disturbing the equilibrium of the molecule. Perhaps also the union of the magnesium atoms by the SO_4 radical in tychite is more difficult to establish than the combination of the two chlorine atoms with magnesium in northupite, which may account for the greater length of time required to make the sulphate compound artificially.

In these compounds, two chlorine atoms in the one and a SO_4 radical in the other play the same rôle, and are isomorphous with one another in the broader sense of the term, namely, that different constituents may enter into similarly constituted molecules without changing the crystalline form. In simple chemical compounds, it is contrary to all experience that a chloride and a sulphate should have the same crystalline form, or be isomorphous with one another. In the salts under consideration, however, it is assumed that some definite arrangement of the large number of sodium, oxygen, carbon and magnesium atoms, by virtue of *mass effect*,* determines the crystalline form of the compounds, and that the rôles played by two chlorine atoms in the one and a SO_4 radical in the other are relatively so unimportant that either of these constituents may enter into the molecule without changing the crystalline form. Whether it is possible to obtain a single crystal containing both the two chlorine atoms and the sulphate radical replacing one another as isomorphous constituents, or to obtain a single crystal with a nucleus of one salt and an external growth, in parallel position, of the other, we are not as yet able to state, but experiments along these lines, to determine to what extent the principles of isomorphism may be applied to so widely different radicals as Cl , and SO_4 , under the influence of mass effect action, will be carried on and form the subject of a later communication. In one experiment, in which the attempt was being made to obtain a product containing both Cl , and the SO_4 radical, a small crop of octahedral crystals was formed which reacted for neither chlorine nor sulphate. In appearance

* Compare *mass effect* action as applied to tourmaline (Penfield and Foote, this Journal (4), vii, pp. 122-124); also to the alunite-jarosite group of minerals (Hillebrand and Penfield, this Journal (4), xiv, pp. 216-220).

the crystals were in every respect like those of the artificial northupite and tychite. As seen with the microscope the crystals were full of inclusions, and, in forming, had evidently enclosed an unusually large amount of amorphous magnesium carbonate precipitate. We assumed at once, and correctly, that the compound would prove to be like northupite and tychite, except in having a CO_3 radical in the place of Cl , and SO_4 , namely, $2\text{MgCO}_3 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3$; see page 222. The analysis, made on a small quantity of the rather impure product, gave almost the theoretical percentage of CO_3 , but the MgO was high and the Na_2O low, which was to be expected. Attempts will be made later to produce this salt in a state of purity, when it will be described more minutely.

Mineralogical Laboratory of the
Sheffield Scientific School of Yale University,
New Haven, Conn., July, 1905.