

ART. XXXIV.—*On the Chemical Composition of Turquoise*;  
by S. L. PENFIELD.

THROUGH the kindness of Mr. Ernest Schernikow of New York City, the writer has recently received a suite of turquoise specimens from deposits in Los Cerillos Mts., New Mexico, and the Crescent Mining District, Lincoln Co., Nevada, and one fragment of exceptionally fine quality from the last named locality was presented with the special request that it should be used for chemical analysis. The material was very fine-grained, of a beautiful robin's-egg blue color, and broke with a smooth fracture. A thin section of the material appeared translucent and almost colorless, and when examined under the microscope, the turquoise seemed to be perfectly uniform, showing no evidence of being made up of two substances, such, for example, as an aluminium phosphate, mixed with a copper salt as coloring material. The material was so fine-grained that no clue as to its crystallization could be made out, other than that it acted somewhat on polarized light. The specific gravity, taken by suspension in the heavy solution, was found to be 2.791.

In considering the chemical composition of turquoise, it should be borne in mind that analyses have been made of only massive, cryptocrystalline fragments, and although they may be selected ever so carefully, no such guarantee of the purity of the material can be given as when, for example, a well crystallized mineral is analyzed. In order to show, however, that turquoise is a material of nearly uniform composition, the new analysis is given below in connection with analyses made by other investigators. Analyses have not been included which show a large proportion of foreign constituents other than silica. The analyses are as follows:

	I. Lincoln Co., Nevada. Penfield.	II. Nichabour, Persia. Church.*	III. Karkaralinsk, Russia. Nicolajew.†	IV. Fresno Co., California. Moore ‡	V. Los Cerillos, Three analyses by	VI. New Mexico. Clarke.§	VII.
P <sub>2</sub> O <sub>5</sub>	34.18	32.86	34.42	33.21	31.96	32.86	28.63
Al <sub>2</sub> O <sub>3</sub>	35.03	40.19	[35.79]	35.98	39.53 <sup>b</sup>	36.88	37.88
Fe <sub>2</sub> O <sub>3</sub>	1.44	2.45 <sup>a</sup>	3.52	2.99	----	2.40	4.07
CuO	8.57	5.27	7.67	7.80	6.30	7.51	6.56
H <sub>2</sub> O	19.38	19.34	18.60	19.98	19.80	19.60	18.49
Insol.	0.93	----	----	----	1.15	0.16	4.20
X	----	MnO .36	----	----	CaO .13	CaO .38	----
	99.53	100.47	100.00	99.96	98.87	99.79	99.83
Sp. gr.	2.79	2.75	2.89	2.86		2.80	

<sup>a</sup> Given as 2.21 per cent FeO.

<sup>b</sup> Includes some Fe<sub>2</sub>O<sub>3</sub>.

\* Chemical News, x, p. 290, 1864.

† Kokscharow's Min. Russland, ix, p. 86, 1884.

‡ Zeitschr. Kryst., x, p. 247, 1884.

§ This Journal, III, xxxii, p. 212, 1886.

In the new analysis the iron was found to exist wholly in the ferric condition, and therefore the iron in Church's analysis, given as FeO in the original article, has been calculated to Fe<sub>2</sub>O<sub>3</sub> to agree with the observations of the author and other investigators.

It is evident from an examination of the foregoing analyses that turquoise is a material which is quite uniform in its chemical composition, so uniform in fact that it does not seem reasonable to consider it as an accidental mixture of an aluminium phosphate and a copper phosphate. The presence of the bivalent element copper, however, in somewhat variable amounts, is not so easily accounted for if we are to consider a copper phosphate as isomorphous with an aluminium phosphate. The small amount of iron is probably isomorphous with the aluminium, and it is to be expected that the iron phosphate would have little effect upon the color of the stone, for the hydrated ferric-phosphate, strengite, and the hydrated ferric-arsenate, scorodite, are both light-colored minerals. The idea that the iron is present as the hydrated oxide, limonite, can scarcely be entertained.

Clarke,\* in discussing the composition of turquoise, states that if the alumina is combined with the phosphoric acid and water to form a molecule 2Al<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub>.5H<sub>2</sub>O, there remains an excess of phosphoric acid and water which forms with the copper a salt of the composition 2CuO.P<sub>2</sub>O<sub>5</sub>.4H<sub>2</sub>O. Turquoise is considered therefore by him as consisting of variable mixtures of the foregoing salts. He regards normal turquoise as the aluminium salt, 2Al<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub>.5H<sub>2</sub>O, which he also expresses as Al<sub>2</sub>HPO<sub>4</sub>(OH)<sub>2</sub>, and "the copper salt, to which the mineral owes its color, is to be considered merely as an impurity." By means of ratios it is quite easy to apply Clarke's theory to the analyses as tabulated on page 346. Taking Al and Fe as a basis, and establishing a ratio of P:Al+Fe:H=1:2:5, as demanded by Clarke's formula for normal turquoise, Al<sub>2</sub>HPO<sub>4</sub>(OH)<sub>2</sub>, the ratio of *the excess of Phosphorus:Cu:the excess of Hydrogen* can then be found. The results of the calculation are as follows:

		I.	II.	III.	IV.	V.	VI.	VII.		
Normal turquoise,	} P	·352	·408	·373	·371	·387	·376	·396		
		} Al+Fe	·704	·816	·746	·742	·774	·752	·792	
			Clarke.	} H	1·760	2·040	1·865	1·855	1·935	1·880
Residues.	} P	·130			·054	·111	·097	·063	·088	·008
		} Cu			·108	·066	·096	·098	·080	·094
			} H	·394	·108	·201	·365	·365	·300	·074

\* Loc. cit.

Taking copper as a basis, the ratios of P : Cu : H in the residues are as follows :

		I.	II.	III.	IV.	V.	VI.	VII.
Residues, } copper } as unity. }	P	1.20	0.82	1.15	0.99	0.78	0.93	0.09
	Cu	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	H	3.65	1.63	2.09	3.72	4.56	3.19	0.90

It is to be taken into consideration that it is a very severe test of a formula to throw all of the errors resulting from possible impurities in the materials and inaccuracies of the analyses upon a single constituent, in the case in hand on the supposed copper salt; but still the ratios of P : Cu : H are so variable that it cannot be considered that turquoise is a mixture of an aluminium salt,  $\text{Al}_2\text{HPO}_4(\text{OH})_2$ , and a hydrated copper phosphate having the definite composition  $2\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  as suggested by Clarke. A compound having the composition  $2\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  demands a ratio of P : Cu : H = 1 : 1 : 4.

An important factor to be taken into consideration is that the hydrogen in turquoise is to be regarded as representing hydroxyl and not water of crystallization, for water is not expelled from the mineral at a low temperature; hence hydroxyl radicals may be considered as playing a part in the chemical composition of the mineral. Considering copper as an essential constituent of turquoise and not as an impurity, two theories naturally suggest themselves: one, that the bivalent copper is isomorphous with, and replaces the bivalent aluminium-hydroxide radical  $[\text{Al}(\text{OH})]''$ ; the other, that the univalent copper-hydroxide radical  $[\text{Cu}(\text{OH})]'$  is isomorphous with the univalent aluminium-hydroxide radical  $[\text{Al}(\text{OH})_2]'$ . The first of these ideas has led to no satisfactory solution of the problem; the second, however, reveals a constancy in the chemical relations of the mineral which can scarcely be regarded as due to accident. The relations in question are shown by combining aluminium and iron with two hydroxyls to form the groups  $[\text{Al}(\text{OH})_2]$  and  $[\text{Fe}(\text{OH})_2]$ , respectively, and copper with one hydroxyl to form the group  $[\text{Cu}(\text{OH})]'$ , and then finding the ratio between the phosphorus and  $[\text{Al}(\text{OH})_2]' + [\text{Fe}(\text{OH})_2]' + [\text{Cu}(\text{OH})]' + \text{Excess of hydrogen}$ . The relations are shown by the ratios derived from the several analyses tabulated on page 346, as follows :

		I.	II.	III.	
P		.482	.462	.484	
$\text{Al}(\text{OH})_2$	.686	} 1.450	.788	} .702	
$\text{Fe}(\text{OH})_2$	.018		.028		.044
$\text{Cu}(\text{OH})'$	.108		.066		.096
H	.638		.450	.478	
				} 1.320	

	IV.	V.	VI.	VII.
P	·468	·450	·464	·404
Al(OH) <sub>2</sub>	·706	·774	·722	·742
Fe(OH) <sub>2</sub>	·036	---	·030	·050
Cu(OH)	·098	·080	·094	·083
H	·638	·572	·582	·387
	} 1·478	} 1·426	} 1·428	} 1·262

Considering  $[Al(OH)_2]' + [Fe(OH)_2]' + [Cu(OH)]' + H'$  as playing the role of a univalent radical R', the ratios of P : R in the several analyses are as follows:

I,	P : R =	·482 : 1·450 = 1 : 3·01
II,	"	" = ·462 : 1·332 = 1 : 2·88
III,	"	" = ·484 : 1·320 = 1 : 2·73
IV,	"	" = ·468 : 1·478 = 1 : 3·16
V,	"	" = ·450 : 1·426 = 1 : 3·17
VI,	"	" = ·464 : 1·428 = 1 : 3·08
VII,	"	" = ·404 : 1·262 = 1 : 3·12
	Average =	1 : 3·02

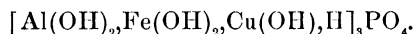
The author can vouch for the purity of the material analyzed by him, as far as it is possible to do so in the case of a cryptocrystalline mineral, and can also testify as to the accuracy of the analysis, and the very close approximation to the exact ratio 1 : 3, between the phosphorus and the sum of the univalent radicals plus the hydrogen, is very suggestive. The ratios in the other analyses approximate as closely to 1 : 3 as might be expected when the character of the material is taken into consideration, and the average of all the ratios is almost exactly 1 : 3. The ratio 1 : 3 is that of phosphorus to hydrogen in ortho-phosphoric acid, H<sub>3</sub>PO<sub>4</sub>. Turquoise may therefore be regarded as a derivative of ortho-phosphoric acid in which the hydrogen atoms are to a large extent replaced by the univalent radical  $[Al(OH)_2]$ ,  $[Fe(OH)_2]$  and  $[Cu(OH)]$ . There seems to be no fixed ratio between the radicals  $[Al(OH)_2]$ ,  $[Fe(OH)_2]$  and  $[Cu(OH)]$ , nor between the sum of the hydroxyl radicals and the hydrogen. In some cases, however, there is an approximation to the ratio 2 : 1 between the sum of the hydroxyl radicals and the hydrogen, as follows:

	$[Al(OH)_2] + [Fe(OH)_2] + [Cu(OH)]$ :	H
II,	·882	: ·450 = 2 : 1·02
III,	·844	: ·478 = 2 : 1·13
VII,	·875	: ·387 = 2 : 0·89

In cases like the foregoing, the composition of turquoise might be considered as a mixture of an aluminium salt,  $H[Al(OH)_2]_2PO_4$ , with the isomorphous molecules  $H[Fe(OH)_2]_2PO_4$  and  $H[Cu(OH)]_2PO_4$ . The molecule  $H[Al(OH)_2]_2PO_4$  is equivalent to Clarke's formula for "normal turquoise,"  $2Al_2O_3 \cdot P_2O_5 \cdot 5H_2O$ , which he also writes  $Al_2HPO_4(OH)_2$ . Adopting

Clarke's suggestion that turquoise contains very finely divided admixtures of iron and copper phosphates as impurities, and also his formula for the pure mineral (*normal turquoise* of Clarke), Groth\* expresses the composition as  $\text{PO}_4\text{Al}_2(\text{OH})_3\cdot\text{H}_2\text{O}_2$  but suggests, however, that the formula is perhaps  $\text{PO}_4\text{H}[\text{Al}(\text{OH})_2]$ .

In conclusion it may be stated that it is the author's belief that copper and the small amounts of iron are to be regarded as constituents of turquoise, rather than as impurities. In support of this idea the constant occurrence of copper, as shown by all the published analyses, may be cited. Furthermore, finely pulverized turquoise is only partially dissolved by boiling in a test tube with hydrochloric acid; hence, if the material contained copper phosphate as an impurity, it would be expected that the copper phosphate would dissolve readily, leaving the basic aluminium phosphate as a pure white residue, while in tests which have been made the insoluble residues have remained blue, from beginning to end of the experiments. Considering the existence in turquoise of the univalent radicals  $[\text{Al}(\text{OH})_2]$ ,  $[\text{Fe}(\text{OH})_2]$  and  $[\text{Cu}(\text{OH})]$ , the composition of the mineral, as shown by the published analyses, may be expressed as a derivative of ortho-phosphoric acid, as follows:



The  $[\text{Al}(\text{OH})_2]$  radical always predominates, but is not present in fixed proportion. Some analyses (II, III, and VII) conform closely to the formula  $[\text{Al}(\text{OH})_2, \text{Fe}(\text{OH})_2, \text{Cu}(\text{OH})]_2\text{HPO}_4$ .

Disregarding the iron, the calculated composition of turquoise for two special cases of isomorphous replacements are given below:

	Analysis I, $[\text{Al}(\text{OH})_2, \text{Cu}(\text{OH}), \text{H}]_3\text{PO}_4$ , Al(OH) <sub>2</sub> :Cu(OH):H=7:1:6. page 346.		Analysis II, $[\text{Al}(\text{OH})_2, \text{Cu}(\text{OH})]_2\text{HPO}_4$ , Al(OH) <sub>2</sub> :Cu(OH)=12:1. page 346.	
P <sub>2</sub> O <sub>5</sub>	34·64	34·18	32·13	32·86
Al <sub>2</sub> O <sub>3</sub>	37·32	36·47 <sup>a</sup>	42·61	42·64 <sup>a</sup>
CuO	8·28	8·57	5·52	5·27
H <sub>2</sub> O	19·76	19·38	19·74	19·34
----	Insol.	0·93	----	MnO 0·36
	100·00	99·53	100·00	100·47

<sup>a</sup> Include the Fe<sub>2</sub>O<sub>3</sub>.

Considering that turquoise is not a crystallized mineral, the agreement between theory and the analyses is certainly as close as could be expected.

\* Tabellarische Uebersicht der Mineralien, 1898, p. 97.

Sheffield Laboratory of Mineralogy and Petrography,  
Yale University, New Haven, June, 1900.