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UNITED STATES GEOLOGICAL SURVEY

J. W. POWELL, DIRECTOR

REPORT OF WORK DONE

IN THE

DIVISION OF CHEMISTRY AND PHYSICS

MAINLY DURING THE

FISCAL YEAR 1885-'86

F. W. CLARKE, Chief Chemist

WASHINGTON
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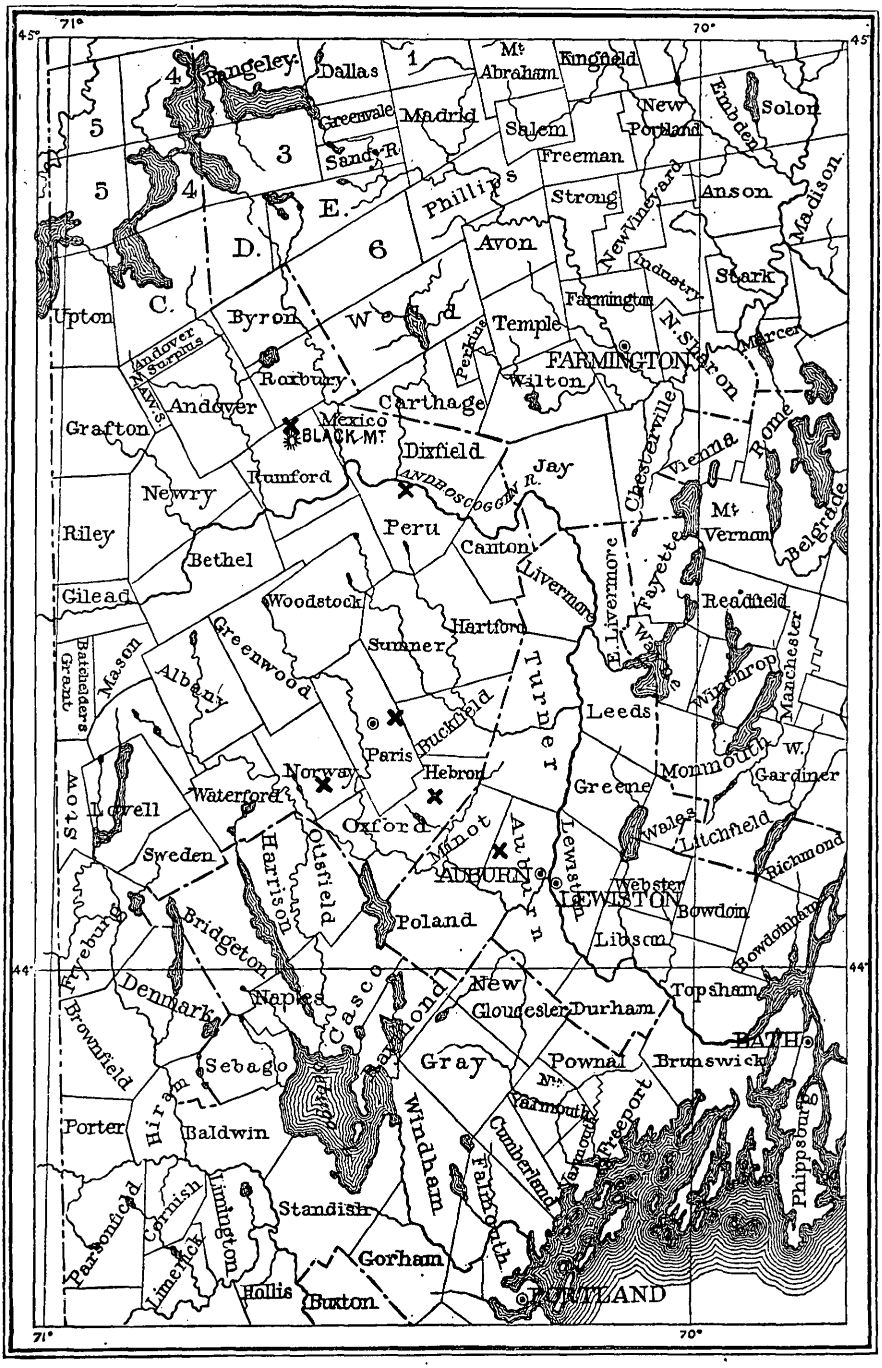
PREFACE.

The present bulletin, like the preceding bulletins numbered 9 and 27, is intended to give a fair representation of the work done in the chemical and physical laboratories of the United States Geological Survey during one fiscal year. It covers, however, only such work as has been actually finished during the stated time, and therefore much material relative to investigations still in progress has been necessarily omitted. One paper, like two others in Bulletin 27, represents the continued coöperation of Prof. V. Strouhal, of Prague, and another bears the names of F. W. Clarke and J. S. Diller as joint authors. Although Mr. Diller is connected with another branch of the Survey, he has rendered many services to this division and has added much to the value of two of the papers herein presented.

The two papers by Dr. Gooch cover investigations which were necessary in the course of a large series of analyses of geyser waters from the Yellowstone Park. The latter are held back for the present, but will appear in a future publication. Mr. Whitfield's research also arose out of similar exigencies. In each case the existing methods of determination were unsatisfactory and not exact enough for our purposes.

F. W. CLARKE,
Chief Chemist.



MAP OF A PORTION OF WESTERN MAINE.

WORK DONE IN THE DIVISION OF CHEMISTRY AND PHYSICS IN 1885-'86.

SCIENTIFIC PAPERS.

RESEARCHES ON THE LITHIA MICAS.

By F. W. Clarke.

I. THE LEPIDOLITES OF MAINE.

In the western part of Maine, along a line running southeasterly from the Rangeley Lakes to a point on the seaboard between Portland and Brunswick, is a series of veins of albitic granite which are noted for the lithia micas and colored tourmalines that they contain. These localities, in the towns of Hebron, Auburn, Norway, Paris, and Rumford, are all within a narrow belt of about 40 miles in length, and with them, as a probable part of the same system, may be classed the spodumene locality in the town of Peru. The northernmost locality is that on Black Mountain, in Rumford; but a few fragments of inferior green tourmaline have been found about five or six miles farther north, in Roxbury, a fact which indicates a prolongation of the belt in that direction. Similarly, a southern extension of the belt is suggested in the region covered by the towns of Pownal, Durham, Yarmouth, and Freeport, a region from which a few specimens of lepidolite have been reported. The total width of the belt, so far as has been observed, appears to be not much over 15 miles.

In general character the several localities are much alike, although in points of minor detail they differ considerably. With the tourmaline and lepidolite, quartz, muscovite, cleavelandite, cassiterite, and amblygonite are always associated; and other minerals, to be specially noted in the separate consideration of the localities, are often found. Some of the differences are doubtless due to the fact that certain localities have been more thoroughly opened up than others, and these would probably be eliminated by more complete exploration. Other differences, however, are notable and characteristic. The accompanying map (Plate I), which shows the geographical distribution of the localities, will be of use for reference during the following discussion.

For convenience we may consider the lepidolites of the several localities separately, beginning with the northernmost and proceeding southward in regular order.

Rumford.—The Rumford locality was discovered several years ago by Mr. E. M. Bailey, of Andover, Maine, but it was not opened up until 1883. It is most easily approached from Andover and is situated on the northern slope of Black Mountain, at an estimated elevation of about a thousand feet above the base. As yet the excavations are merely superficial, although they are sufficient to show the general character of the deposit. A part of the lepidolite, which is very abundant, is fairly pure, lilac purple in color, and finely granular; but the larger portion of the mineral is coarser in structure, reddish, and thickly sprinkled with small, opaque, red tourmalines. The color of the latter is very rich, and some are found in radiated masses of considerable size; but so far no true gem material has been obtained at the locality. The appearance of the associated lepidolite and tourmaline is strikingly characteristic and resembles nothing from the other localities of the region. Green tourmaline is found quite sparingly, and so also are amblygonite and tinstone. The spodumene, however, is one of the notable features of the deposit, occurring in masses of very great size. Faces of this mineral over a meter in length can be observed at several points along the vein. At the other lepidolite localities spodumene is comparatively scarce. An analysis of the granular purple lepidolite gave Mr. R. B. Riggs the following results:

	I	II
SiO_2	51.52	51.32
Al_2O_3	25.89	26.35
Fe_2O_3	.31	
FeO	Undet.	
MnO	.20	....
CaO	.16	....
MgO	.02	....
Li_2O	4.87	4.93
Na_2O	1.18	.94
K_2O	11.00	11.02
H_2O	.88	1.02
F	5.80	5.91
	101.83	
Less oxygen	2.44	
	99.39	

In the ordinary analysis no cæsium nor rubidium could be found; but a bare trace of the the latter was shown spectroscopically in an examination of the alkalies concentrated from 150 grammes of the mineral. In all the analyses the water was determined directly by means of the

Gooch tubulated crucible. Lithia was estimated by the new method devised by Dr. Gooch and described in another part of this bulletin. The fluorine was determined by the old Berzelius process.

Paris.—The famous locality known as Mount Mica, which lies about a mile eastward from the village of Paris, was discovered in 1820 by Messrs. E. L. Hamlin and Ezekiel Holmes. Since that time large excavations have been made in search of mica and of gem tourmalines, and the locality is one of those most noted among mineral collectors. It has been thoroughly described by various writers, especially by Dr. A. C. Hamlin in his little book The Tourmaline.[1] Quite naturally, on account of the long continued explorations, the list of species found at Mount Mica is much fuller than that for any of the other deposits; and, according to Mr. S. R. Carter, who has supervised much of the excavation and made large personal collections, it embraces the following minerals: *Tourmaline*, black, green, red, blue, white, and yellow; *Beryl*, green, white, and yellow; *Quartz*, rose, yellow, smoky, and crystallized; *Garnet; Zircon; Albite*, cleavelandite; *Orthoclase; Spodumene; Muscovite; Biotite; Lepidolite; Autunite; Apatite*, green, blue, and crystallized; *Cookeite; Brookite; Childrenite; Yttrocerite; Amblygonite; Kaolinite; Halloysite; Cassiterite; Löllingite; Triphylite; Pyrite;* and *Tantalite* (?).

The lepidolite occurs both in the purple, granular form, and also broadly foliated like muscovite. The latter variety was analyzed by Mr. Riggs, and the results may well be compared with those obtained by Berwerth[2] and by Rammelsberg:[3]

	Riggs.		Berwerth.	Rammelsberg.
	I.	II.		
SiO_2	50.92	50.68	50.39	52.61
Al_2O_3	24.99		28.19	28.43
Fe_2O_3	.30			
FeO	.23			
MnO	Trace		Trace	Mn_2O_3 Trace
Li_2O	4.11	4.29	5.08	4.09
Na_2O	2.23	2.00		.79
K_2O	11.50	11.25	12.34	10.89
Cs_2O	Trace			
Rb_2O	Trace			
H_2O	1.92	2.00	2.36	.22
F	6.29	6.31	5.15	5.19
	102.49		103.51	102.22
Less oxygen	2.64		2.17	2.19
	99.85		101.34	100.03

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[1] Published by James R. Osgood & Company, Boston, 1873, 12°, 107 pp.

[2] Zeit. Kryst. Min., 2, p. 523.

[3] See Third Supplement to Dana's System of Mineralogy p. 79,

Hebron.—About 7 miles southeast of Mount Mica is the well known locality in Hebron, which, however, because of legal complications in the title to the land, has been but little worked. All the exploration, so far, has been superficial; and yet many fine specimens of green and red tourmaline, cassiterite, amblygonite, cookeite, beryl, apatite, and childrenite have been obtained. The lepidolite of this locality is of the ordinary purple, coarsely granular kind, but is especially interesting on account of the fact that it has supplied chemists with considerable quantities of the rare metals cæsium and rubidium. The existence of these elements in lepidolite was first pointed out by Johnson and Allen,[1] who were working on the Hebron mineral; and yet no complete analysis of the latter seems so far to have been published.

The following results were obtained by Mr. Riggs:

	I.	II.
SiO_2	48.80	48.68
Al_2O_3	28.29	28.71
Fe_2O_3	.29	
FeO	.09	
MnO	.08	....
CaO	.10	....
MgO	.07	....
Li_2O	4.40	4.58
Na_2O	.72	.76
K_2O	12.35	12.06
Rb_2O		
Cs_2O		
H_2O	1.66	1.80
F	4.96	5.19
	101.81	
Less oxygen	2.02	
	99.79	

In this case the potassium, rubidium, and cæsium were weighed together as chlorides and the chlorine was subsequently determined. The percentages given, 12.35 and 12.06, respectively, therefore represent the actual oxides present, and not merely a computation of all as potash from the platinchloride. In the one case we have 10.34 of metal to 2.01 of oxygen, while in the second analysis we have the ratio 10.98

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[1] Am. Jour. Sci. (II), XXXV, p. 94.

to 1.98. If cæsium and potassium only were present these would give by indirect calculation the following proportions of the two metals:

	I.	II.
K_2O	11.47	11.40
Cs_2O	.88	.66
	12.35	12.06

The cæsia and rubidia present, therefore, must be less than the figures given for Cs_2O.

Associated with the Hebron lepidolite there have been found specimens of red and green tourmaline, which, preserving their crystalline form, have undergone alteration into a softer mineral of an opaque, talcose appearance. Some of this material so derived from tourmaline has been supposed to be lepidolite; and, as it was possible that a study of it might be of interest, an analysis of a pink specimen, originally rubellite, was made by Mr. Riggs. The specific gravity, as determined by Mr. T. M. Chatard, was 2.87. Analysis is as follows:

SiO_2	43.90
Al_2O_3	38.71
Fe_2O_3	.58
FeO	.25
MnO	.04
CaO	.41
MgO	.05
Na_2O	1.05
K_2O	10.92
H_2O	4.25
F	None
B_2O_3	Strong trace
	100.16

These results show clearly that the alteration product is not lepidolite, but damourite, a fact which could hardly be altogether unexpected.

Auburn.—In the western part of this town, near the Minot line, there are two localities, less than half a mile apart, yielding lepidolite with the associated minerals. The one longest known is small and apparently unimportant, while the other, lying about southeast of the first, upon the farm of Mr. G. C. Hatch, has been thoroughly opened. It has yielded a large number of gem tourmalines, mostly of the paler greenish, lilac, or lavender colors, unusually fine crystallizations of apatite, and perhaps the best crystallizations of lepidolite so far known.[1] Cookeite, orthoclase, albite, cassiterite, muscovite, biotite, beryl, garnet, quartz,

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[1] For a description of this locality, see G. F. Kunz, Am. Jour. Sci. (III), XXVII, p. 303.

and amblygonite are among the other species here found. The lepidolite occurs in the ordinary purple, coarsely granular form, and also in remarkable perfection as a border upon muscovite, the broad plates of the latter being practically encircled by aggregations of small crystals of the lithia mica. Some specimens of this type have also been found at Paris, but the Auburn examples are much finer than those from other localities. The accompanying illustration (Fig. 1) shows the peculiar association of the two minerals.

FIG. 1. Border of lepidolite on muscovite.

As it was hoped that this mode of occurrence of lepidolite might throw some light upon its genesis, three analyses of material from Auburn were made by Mr. Riggs: first, of the common granular variety; secondly, of the border upon muscovite; and, thirdly, of the muscovite itself from the center of the second specimen. The results were as follows, the lithia being determined by the old phosphate method;

	I. Granular lepidolite.			II. Border on muscovite.		III. Muscovite.
SiO_2	51.11			49.62		44.48
Al_2O_3	25.26			27.20		35.70
Fe_2O_3	.20			.31		1.09
FeO	.07			.07		1.07
MnO	.17			.55		Trace
CaO	.12			....		.10
MgO	.01			....		Trace
Li_2O	4.78	5.17		4.50	4.17	Trace
Na_2O	1.52	1.35		2.10	2.25	2.41
K_2O	10.51	12.21		8.03		9.77
Rb_2O	1.29			2.44		....
Cs_2O	.45			.72		....
H_2O	.88	1.01		1.52		5.50
F	6.57	6.67	6.60	5.45	5.78	.72
	102.94			102.51		100.84
Less oxygen	2.76			2.29		.30
	100.18			100.22		100.54

In these analyses the determinations of cæsia and rubidia are to be considered merely as rough approximations. The cæsium was separated as stannichloride, and the rubidium and potassium were computed from the amount of chlorine in the mixed chlorides of the two metals. In the oxides K_2O, Rb_2O, and Cs_2O, taken together, the actual ratio of metal to oxygen in analyses I and II is as follows:

	I.		II.
Metal	10.32	10.26	9.57
Oxygen	1.93	1.95	1.62
$(KRbCs)_2O$	12.25	12.21	11.19

Norway.—This locality, which has been but little opened, is about seven miles from Mount Mica, in a southerly direction. With the lepidolite are associated, as usual, quartz, the feldspars, the micas, cassiterite, lithiophilite, beryl, &c., and also a peculiar rose red clay, derived from some other species by alteration. Most of the colored tourmaline is of a peculiar dark oily green tint, and the lepidolite is partly of a coarsely granular white variety and partly of a brownish, very finely granular sort.

Analyses of both varieties by Mr. Riggs came out as follows:

	White.		Brown.
SiO_2	49.52	49.45	50.17
Al_2O_3	28.80		25.40
Fe_2O_3	.40		.87
FeO	.24		.45
MnO	.07		.23
CaO	.13		Undet.
MgO	.02		Undet.
Li_2O	3.87		4.03
Na_2O	.13		
K_2O	8.82	12.70	13.40
Rb_2O	3.73		
Cs_2O	.08		
H_2O	1.60	1.85	2.02
F	5.18	5.39	5.05
	102.59		101.62
Less oxygen	2.18		2.13
	100.41		99.49

The analysis of the brown variety was only partial.

The lithia was determined by the phosphate method, while, as in the case of the Auburn material, the cæsia and rubidia estimations are merely approximative. The actual ratios between metal and oxygen in the potassium group, as found in the two experiments upon the white lepidolite, are subjoined:

Metal	10.83	10.91
Oxygen	1.80	1.79
$(KRbCs)_2O$	12.63	12.70

The fact that this lepidolite is the richest of the series in these rare metals becomes doubly interesting when we remember that a beryl from the same or a nearly adjacent locality gave Penfield 1.66 per cent. of cæsia.[1]

Of the rose-red clay, previously mentioned, a partial analysis was published in Bulletin No. 9, U. S. Geol. Surv. The following complete analysis by Mr. Riggs is better, and shows, in spite of some little non-uniformity of composition in the material, that it is to be classed most definitely as cimolite:

SiO_2	66.86
Al_2O_3	22.23
Fe_2O_3	.47

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[1] Am. Jour. Sci. (III), XXV, p. 28. The Hebron beryl contains 2.92 per cent.

FeO	.18
MnO	.07
CaO	.42
MgO	.33
Li_2O	.29
Na_2O	.46
K_2O	.18
H_2O	8.26
F	.06
	99.81
Less oxygen	.02
	99.79

Formula, $Al_2H_4(SiO_3)_5$.

It is not easy to determine, from the specimens at hand, from what species this clay has been derived.

DISCUSSION OF RESULTS.

The foregoing analyses of the Maine lepidolites cover several distinct types of the mineral from five different localities, and yet they indicate a very great constancy or uniformity of composition. For convenience of comparison, we may tabulate the results, using mean values whenever two determinations of a constituent have been made. Two exceptions to this rule, however, have been adopted, namely, to use the higher determinations for silica and the lower for fluorine, because of the known direction of the experimental errors in the analytical processes. Slight loss of silica, when fluorine is present, is difficult to avoid; and so also slight impurities in the calcium fluoride can hardly be eliminated. With these qualifications the analyses may be stated as follows:

	Rumford, purple.	Paris, foliated.	Hebron, granular.	Auburn.		Norway.	
				Border.	Granular.	White.	Brown.
SiO_2	51.52	50.92	48.80	49.62	51.11	49.52	50.17
Al_2O_3	25.96	24.99	28.30	27.30	25.26	28.80	25.40
Fe_2O_3	.31	.30	.29	.31	.20	.40	.87
FeO	Undet.	.23	.09	.07	.07	.24	.45
MnO	.20	Trace	.08	.55	.17	.07	.23
CaO	.16	Trace	.10	....	.12	.13	Undet.
MgO	.02	Trace	.07	....	.01	.02	Undet.
Li_2O	4.90	4.20	4.49	4.34	4.98	3.87	4.03
Na_2O	1.06	2.11	.74	2.17	1.43	.13	13.40
K_2O	11.01	11.38	12.21	8.03	10.51	8.82	
Rb_2O	....	Trace		2.44	1.29	3.73	
Cs_2O	....	Trace		.72	.45	.08	
H_2O	.95	1.96	1.73	1.52	.94	1.72	2.02
F	5.80	6.29	4.96	5.45	6.57	5.18	5.05
	101.89	102.38	101.86	102.52	103.11	102.71	101.62
Less oxygen	2.44	2.64	2.02	2.29	2.76	2.18	2.13
	99.45	99.74	99.84	100.23	100.35	100.58	99.49

With this table may be advantageously compared the following analyses of lepidolite from three foreign localities:[1]

	Rozena.		Cornwall, Rammelsberg.	Juschakova.	
	Berwerth.	Rammelsberg.		Rosales.	Rammelsberg.
SiO_2	50.98	51.32	51.70	48.92	50.26
Al_2O_3	27.80	26.00	26.76	19.03	21.47
Fe_2O_3	....	....	....	....	....
FeO	.05	....	....	....	....
Mn_2O_3	....	1.30	1.29	5.59	5.36
CaO	....	....	.40	.14	....
MgO	....	....	.24	....	....
Li_2O	5.88	3.87	1.27	2.77	4.88
Na_2O	....	.96	1.15	2.23	.54
K_2O	10.78	9.98	10.29	10.96	11.08
H_2O	.96	.57	....	....	.66
F	7.88	7.18	7.12	10.44	8.71
Cl	....	....	....	1.31	1.16
P_2O_5	.05	....	.16	....	....
	104.38	101.18	100.38	101.39	104.12
Less oxygen	3.37	3.02	2.99	4.68	3.93
	101.01	98.16	97.39	96.71	100.19

Few other lepidolite analyses are worth quoting, except possibly Cooper's analysis of the Rozena mineral, in which he found 0.24 per cent. of rubidia and a trace of cæsia.[2] The essential identity of the material from Maine, Rozena, and Cornwall is thus made clear, while the lepidolite from Juschakova is different in its large percentage of manganese, its higher fluorine, and its trace of chlorine. In the last named mineral of course the manganese replaces an equivalent amount of alumina, and the function of chlorine is the same as that of fluorine. In the other analyses, to speak in general terms, the water and fluorine vary somewhat reciprocally, suggesting the ordinary replacement of the latter element by hydroxyl. With this assumption, if it may be called so, the formula of lepidolite may be written thus:

$$Al_2(SiO_3)_3F_2LiK;$$

a formula which has long had general acceptance, but which is now put upon a surer basis by the wider range of analyses. It corresponds to the following theoretical composition:

	Calculated.		Found (Riggs).
SiO_2	49.18	SiO_2	48.80 to 51.52
Al_2O_3	27.87	Al_2O_3	24.99 to 28.80
Li_2O	4.09	Li_2O	3.87 to 4.98
K_2O	12.81	$(NaKRbC_5)_2O$	12.07 to 13.68
F	9.84	(F,H_2O)	6.69 to 8.25

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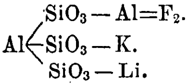
[1] See Dana's System of Mineralogy, p. 315, and Third Supplement, pp. 78, 79.

[2] Pogg. Ann., pp. 113, 343.

Most of the variations from theory are no greater than we should expect to find them with material so difficult to secure in absolute purity as lepidolite. The granular structure of the species is peculiarly favorable to the presence of inclusions of foreign matter, such as albite, for example, to which latter impurity some of the soda found in the analyses is very probably due. The greatest difference is in the case of fluorine, although the foreign analyses—notably Rammelsberg's analysis of the Juschakova mineral—contain very nearly the full theoretical amount. If, however, the fluorine is present in the univalent group AlF_2, it is possibly replaceable in part by the similar group AlO, a supposition which easily accounts for all the variations. With this supposition it becomes a simple matter to write a probable structural formula for lepidolite, as follows:



$$Al\left\langle\begin{array}{l} SiO_3-Al=F_2. \\ SiO_3-K. \\ SiO_3-Li. \end{array}\right.$$

Thus the mineral is regarded as a definite substitution derivative of the normal aluminum metasilicate $Al_2(SiO_3)_3$, one atom of Al having been replaced by the three univalent factors represented above. Another view of its structure is given at the close of this paper.

II. THE IRON LITHIA MICAS OF CAPE ANN.

In the granite quarries of Rockport, Massachusetts, near the extremity of Cape Ann, there are occasional veins of feldspathic character which contain, along with the ordinary constituents of such veins, the rare minerals danalite, fergusonite, cyrtolite, amazon stone, and certain remarkable micas. One of the latter, cryophyllite, was described by Cooke in 1867,[1] who also analyzed an associated "lepidomelane," to which Dana afterwards gave the name of annite. The vein from which Cooke obtained his material was long ago blasted away or covered up, but other veins of like nature are still accessible, and from one of them the micas examined in this laboratory were obtained. They were collected for the United States National Museum by the original discoverer of the locality, Mr. W. J. Knowlton, and were, to all outward appearance, identical with the micas described by Cooke. The analyses, however, reveal notable differences between the older and the newer material and add great interest to the micas of the locality.

In the collection furnished by Mr. Knowlton two micas were clearly recognizable, the one a dark greenish black lithia mica, presumably cryophyllite, and the other a black, brilliant lepidomelane. In some specimens the cryophyllite formed a border of small crystals around the broader plates of annite, precisely as in the association of lepidolite and

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[1] Am. Jour. Sci. (II), XLIII, p. 217.

muscovite at Auburn. The resemblance in this point is curiously striking, only that the Rockport specimens are less conspicuous than those from Auburn, since they lack the contrast of color by which the latter are characterized.

The lithia mica, or cryophyllite, varies considerably in external character, and three well marked types of it were selected for analysis: first, the broadly foliated, brilliant, blackish green mica, which showed no trace of alteration; secondly, a paler, dull green, less lustrous variety, apparently somewhat altered upon the surface; thirdly, an aggregation of minute six-sided prisms, so small as to give the mineral an almost granular appearance, similar to an ordinary dark green chlorite. The analyses were made by Mr. Riggs, who used the Gooch process for separating lithia and Berzelius's method for the fluorine. The results were as follows:

	Foliated.		Altered.		Granular.	
SiO_2	51.96	51.74	51.46	51.35	52.17	52.07
Al_2O_3	16.89		16.22		16.39	
Fe_2O_3	2.63		2.21		4.11	
FeO	6.35	6.29	7.66	7.60	6.08	5.90
MnO	.24		.06		.32	
CaO	.12		Trace		Trace	
MgO	.03		.17		Trace	
Li_2O	4.93	4.80	4.83	4.78	5.03	4.95
Na_2O	.92	.81	.95	.82	.60	.66
K_2O	10.66	10.73	10.65	10.65	10.54	10.42
H_2O	1.22	1.40	1.06	1.18	1.43	1.48
F	6.78	6.86	7.44	7.60	7.02	7.20
	102.73		102.71		103.69	
Less oxygen	2.86		3.11		2.95	
	99.87		99.60		100.74	

These results demonstrate the essential identity of the three specimens, but do not sharply correspond with the figures given by Cooke. In mean, using, as in the case of the lepidolites, the maximum silica and minimum fluorine determinations, they may be compared with Cooke's analysis as follows:

	Riggs.	Cooke.
SiO_2	51.86	51.49(+1.97)
Al_2O_3	16.50	16.77
Fe_2O_3	2.98	1.97
FeO	6.65	7.98
MnO	.21	Mn_2O_3 .34
CaO	.04	....
MgO	.07	.76
Li_2O	4.89	4.06
Na_2O	.79	Trace
K_2O	10.61	13.15. Tr. Rb_2O
H_2O	1.29	....
F	7.08	SiF_4 3.42. F, 2.49
	102.97	99.94
Less oxygen	2.98	
	99.99	

It will be seen at once that Cooke's mineral contains only about one-third of the fluorine found in the later analyses and that it runs notably higher in silica and alkalies. In general terms the same mineral is represented by both analyses, with the presumption as to purity in favor of the specimens examined by myself. If we assume that Cooke's material contained a slight isomorphous admixture of some other micaceous species poor in fluorine, the most important difference is accounted for.

Inasmuch as some writers have been inclined to identify cryophyllite with zinnwaldite, a comparison of the two species may be instructive. The published analyses of zinnwaldite vary widely, especially in the amounts of iron; but the older figures are subject to doubt as regards the relative proportions of ferrous and ferric oxides. Two comparatively recent analyses by Berwerth and Rammelsberg, however, agree fairly well with each other, although, compared with former determinations, they run low in iron. The comparison between the analyses is subjoined:

	Cryophyllite, Riggs.	Zinnwaldite.	
		Berwerth.[1]	Rammelsberg.[2]
SiO_2	51.86	45.87	46.44
Al_2O_3	16.50	22.50	21.84
Fe_2O_3	2.98	.66	1.27
FeO	6.65	11.61	10.19
MnO	.21	1.75	1.57
CaO	.04	....	....
MgO	.07	....	.18
Li_2O	4.89	3.28	3.36
Na_2O	.79	.42	.54
K_2O	10.61	10.46	10.58
H_2O	1.29	.91	1.04
F	7.08	7.94	7.62
P_2O_5	....	.08	....
	102.97	105.48	104.63

[1] Zeit. Kryst. und Min., II, p. 525.

[2] See Third Supp. to Dana's Syst. Min., p. 79.

Reduced to empirical formulæ these analyses give two quite different ratios, which, however, do not admit of very simple expression:

Cryophyllite: $FeH_3K_3Li_4Al_4F_4(SiO_3)_{10}$;
or, $Al_2(SiO_3)_5F_2R'_6$.
Zinnwaldite: $Fe_3H_2K_4Li_4Al_8F_8(SiO_3)_{14}$;
or, $Al_4(SiO_3)_7F_4R'_8$.

The further consideration of these formulæ may be deferred until the latter portion of the paper. For present purposes they serve to show the non-identity of the two minerals.

For the lepidomelane, or annite, of Rockport, quite unexpected results were obtained. The material analyzed by Mr. Riggs was black, brilliant, broadly foliated, and apparently very pure. Upon the specimens examined some purple fluorite was visible. The water estimations were directly made with the Gooch tubulated crucible.

	Annite.	
	Riggs.	Cooke.
SiO_2	31.96	39.55
TiO_2	3.42	
Al_2O_3	11.93	16.73
Fe_2O_3	8.06	12.07
FeO	30.35	17.48
MnO	.21	Mn_2O_3 .60
CaO	.23	
MgO	.05	.62
Li_2O	Trace	.59
Na_2O	1.54	Trace
K_2O	8.46	10.66
H_2O	4.25	1.50
F	Trace	SiF_4 .62
	100.46	100.42

It is at once evident that two entirely distinct micas are here represented, and the question is raised as to whether the Rockport granites may not contain a series of complex isomorphous mixtures. Cooke, indeed, pointed out the isomorphism of cryophyllite with the lepidomelane which he had analyzed, and showed that the lithia and the fluorine in the latter were probably due to admixtures of the former. We now see that more than two micas are involved in the problem, and the difficulty of establishing accurate formulæ for the several species becomes enormously increased. For the present, approximate formulæ only can be assigned, involving various assumptions and representing probabilities rather than complete interpretations of the facts. If we unite the groups TiO_2 and SiO_2 in our annite and regard the ferric iron as belonging partly with the alumina and as partly having been the result of oxidation from the ferrous state, we have the two following general formulæ for the two analyses:

Annite, Cooke, $R'_8Al_4(SiO_4)_5$.
Annite, Riggs, $R'_{14}Al_2(SiO_4)_5$.

For the latter, the equivalent of R' is approximately $K_2H_4Fe''_4$; and for the former it is $K_2H_2Fe''_2$. These values correspond to the following percentage compositions:

	Cooke.	Riggs.
SiO_2	39.5	36.6
Al_2O_3	26.8	12.4
FeO	18.9	35.1
K_2O	12.4	11.5
H_2O	2.4	4.4
	100.0	100.0

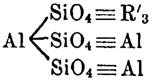
Attention has already been called to the fact that some specimens of cryophyllite are borders upon plates of annite, precisely as the lepidolite of Auburn is arranged about nuclei of muscovite. It accordingly becomes quite probable that a similar relation connects the two pairs of minerals, and upon that relation the formulæ so far assigned shed some light. In each case we have a mineral with metasilicate ratios implanted upon an orthosilicate, and a derivability of the one from the other is strikingly suggested. Structural analogies also appear, for in each pair we have a common type of nucleus, which may be represented as follows:

Muscovite nucleus, $Al(SiO_4)_3$.	Annite nucleus, $Al_2(SiO_4)_5$.
Lepidolite nucleus, $Al(SiO_3)_3$.	Cryophyllite nucleus, $Al_2(SiO_3)_5$.

The development of complete structural formulæ from these nuclei is rendered difficult by our ignorance of the part which fluorine plays in such compounds. In the formula previously assigned to lepidolite the fluorine is represented as combined with aluminum in the univalent group AlF_2; but a similar representation becomes difficult, if not impossible, in the case of the two iron micas. A different solution of the problem must therefore be sought, and it probably is to be found by an application of the generally recognized principle that fluorine and hydroxyl can replace each other isomorphously.

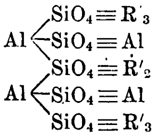
If, now, we start with orthosilicic acid $Si(OH)_4$ and regard the hydroxyl groups as successively replaceable by atoms of fluorine, we can conceive of a series of acids ranging from $Si(OH)_4$ to SiF_4; and by the aid of such a supposition many of the fluoriferous silicates may be rationally explained. For example, the acid $SiF(OH)_3$ may be considered, and its nucleus $SiFO_3$, a trivalent residue, may be applied to the discussion of the lithia micas. Upon this supposition the empirical formula for cryophyllite, $Al_2F_2Si_5O_{15}R'_6$, and the similar formula for lepidolite, $Al_2F_2Si_3O_9R'_3$, become curiously significant, especially when they are written out in contrast with two other formulæ, as in the subjoined scheme:

Muscovite.



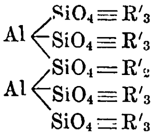
$$Al\left\langle\begin{array}{l}SiO_4\equiv R'_3\\ SiO_4\equiv Al\\ SiO_4\equiv Al\end{array}\right.$$

Annite (Cooke).



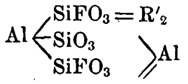
$$\begin{array}{ll} & SiO_4\equiv R'_3\\ Al & SiO_4\equiv Al\\ & SiO_4\equiv R'_2\\ Al & SiO_4\equiv Al\\ & SiO_4\equiv R'_3\end{array}$$

Annite (Riggs).



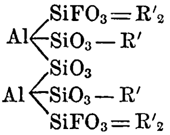
$$\begin{array}{ll} & SiO_4\equiv R'_3\\ Al & SiO_4\equiv R'_3\\ & SiO_4=R'_2\\ Al & SiO_4\equiv R'_3\\ & SiO_4\equiv R'_3\end{array}$$

Lepidolite.



$$Al\left\langle\begin{array}{l}SiFO_3=R'_2\\ SiO_3\\ SiFO_3\end{array}\right\rangle Al$$

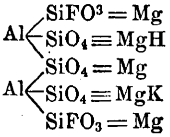
Cryophyllite.



$$\begin{array}{ll} & SiFO_3=R'_2\\ Al & SiO_3-R'\\ & SiO_3\\ Al & SiO_3-R'\\ & SiFO_3=R'_2\end{array}$$

To the zinnwaldite, as represented by the newer analyses, no probable structure is assignable, and it is very possibly a mixture of isomorphous species. Indeed, the old analyses indicate great variability in its composition, and it needs to be more thoroughly studied, not only for itself, but also in its relations to whatever other micas may be associated with it. The matter of association can never, in the study of the micas, be safely neglected.

Although the formulæ herein assigned to annite and cryophyllite are purely provisional and approximative, at least as regards the values ascribable to R′, it may be set down as practically certain that the ratios between the sesquioxides and the silica are correctly given. These ratios are the ratios of phlogopite, with which, therefore, rather than with the lepidomelanes and biotites, the Rockport micas are chemically to be classed. Zinnwaldite is already so classed by Tschermak and others, and cryophyllite falls easily into the same category. A typical phlogopite is fairly represented by the subjoined formula:



$$\begin{array}{l} \mathrm{Al}\begin{cases} \mathrm{SiFO^3} = \mathrm{Mg} \\ \mathrm{SiO_4} \equiv \mathrm{MgH} \\ \mathrm{SiO_4} = \mathrm{Mg} \end{cases} \\ \mathrm{Al}\begin{cases} \mathrm{SiO_4} \equiv \mathrm{MgK} \\ \mathrm{SiFO_3} = \mathrm{Mg} \end{cases} \end{array}$$

THE MINERALS OF LITCHFIELD MAINE.

By F. W. Clarke.

In Kennebec County, Maine, along and near the boundary between the towns of Litchfield and West Gardiner, are scattered many bowlders of an elæolite rock. For many years these have yielded to collectors of minerals superb specimens of blue sodalite, yellow cancrinite, and zircon; but although the parent ledge appears at several points, it seems nowhere to have been opened. In addition to the minerals already mentioned, the bowlders contain albite, lepidomelane, a black mineral resembling columbite, a flesh colored mineral which has been called indiscriminately elæolite or cancrinite, and a massive alteration product known to local collectors under the provisional name of "white sodalite." Although specimens from the locality are widely distributed in cabinets, some of the minerals seem to have been but partially described; and I have therefore thought it worth while to study them somewhat closely. The supposed columbite I have not examined, for want of material; the zircon I have omitted, since it has been sufficiently studied by Gibbs;[1] but the sodalite and cancrinite, although they had been well analyzed by Whitney,[2] I have included in my investigation, for reasons which will appear below.

ELÆOLITE.

This species occurs abundantly in Litchfield and West Gardiner in characteristic, dark gray, cleavable masses of strong greasy luster. Since it is the typical mineral of its group and as I can find no published analysis of it from this locality, the following results may have value as a matter of record:

H_2O	.86
SiO_2	43.74
Al_2O_3	34.48
CaO	Trace
MgO	Trace
K_2O	4.55
Na_2O	16.62
	100.25

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[1] Pogg. Ann., LXXI, 559.

[2] Pogg. Ann., LXX, 431.

The specimen analyzed contained minute inclusions of black mica, but not enough of them to notably affect its composition. The analysis agrees fairly well with the published analyses of elæolite from other places.

CANCRINITE.

This mineral is one of the most abundant and characteristic at the locality and varies considerably in appearance. Two analyses of it were made by Whitney, one of the yellow variety, the other of a greenish modification. I have myself seen nothing to answer to the latter description, but have selected three typical samples for investigation. They may be briefly described and indicated as follows:

A. Bright orange yellow, with strong luster and cleavage, transparent in thin fragments.

B. Dirty pale yellow, less lustrous, highly cleavable, also transparent in thin fragments.

C. Bright yellow, granular—the commonest variety.

For ease of comparison I have tabulated the analyses side by side with Whitney's, indicating his yellow cancrinite by D and his greenish variety by E. The carbonic acid determinations were made for me by Mr. R. B. Riggs, who used the Gooch tubulated crucible and collected the gas evolved directly in a potash bulb.

	A.	B.	C.	D.	E.
SiO_2	36.29	35.83	37.22	37.42	37.20
Al_2O_3	30.12	29.45	28.32	27.70	27.59
Mn_2O_3	Trace	Trace	Trace	.86	.27
Fe_2O_3	Trace	Trace	Trace		
CaO	4.27	5.12	4.40	3.91	5.26
Na_2O	19.56	19.33	19.43	20.98	20.46
K_2O	.18	.09	.18	.67	.55
MgO	......	......	.07	......	......
H_2O	2.98	3.79	3.86	2.82	3.28
CO_2	6.96	6.50	6.22	5.95	5.92
	100.36	100.11	99.70	100.31	100.53

It will at once be observed that cancrinite A, which, from its appearance, was presumably the purest type of the mineral, is the highest of my series in carbonic acid and the lowest in water. It is also the highest in soda and alumina. Whitney's two analyses show more potash than mine, but in other respects run fairly near C, which, as I have said, represents the commonest and probably the least pure variety. But, in order to understand the variations better, we must consider the flesh colored mineral referred to in my introductory paragraph, which, as I have said, has been called indiscriminately elæolite or cancrinite, according to the fancy of the collector. It sometimes occurs in specimens of considerable size, is lustrous and cleavable, and to the eye appears perfectly homogeneous. An analysis gave the following results, the carbonic acid, as in the other cases, being determined by Mr. Riggs:

SiO_2	38.93
Al_2O_3	32.52
CaO	2.47
Na_2O	17.02
K_2O	3.23
H_2O	2.83
CO_2	2.95
	99.95

These figures plainly indicate that the mineral is a mixture of elæolite and cancrinite, but do not show whether the mixture is mechanical or due to isomorphism. To determine this point, Mr. J. S. Diller kindly undertook a microscopic examination of the material, comparing it in thin sections with the elæolite and cancrinite B, from the specimens of which portions were previously analyzed. He found the mineral to be a merely mechanical commingling of the two species, in nearly equal proportions, and later he succeeded in separating them by means of Sonstadt's solution. This fact, considered together with the apparent homogeneity of the material, renders it probable that the variations in composition of the cancrinite are due to small admixtures of elæolite, and that Whitney's specimens were rather more so contaminated than mine. Still, the entire series of cancrinite analyses are fairly concordant and confirmatory of one another. In discussing the formula of the mineral, however, analysis A will be given preference.

SODALITE.

On account of its beauty and its intense blue color, this mineral, as it occurs at Litchfield, is a favorite among collectors. It is now somewhat scarce, at least in large or compact specimens, and it ought to be carefully searched for in place. It often occurs intermingled with cancrinite, forming beautifully mottled masses, and also is associated intimately with the white, massive alteration product to be described later. The following analysis was made partly for comparison with Whitney's and partly to aid in the study of the accompanying white mineral:

	Clarke.	Whitney.	
SiO_2	37.33	37.30	37.63
Al_2O_3	31.87	32.88	30.93
Fe_2O_3	....	......	1.08
Na_2O	24.56	23.86	25.48
K_2O	.10	.59	Undet.
Cl	6.83	6.97	Undet.
H_2O	1.07	....	....
	101.76	101.60	
Deduct O=Cl	1.54		
	100.22		

In my analysis iron was not looked for, because the ignited alumina, which should have contained it if present, was perfectly white. Otherwise the analyses agree tolerably well.

HYDRONEPHELITE, A NEW SPECIES.

Intimately associated with the sodalite is the white alteration product mentioned in the last paragraph. So close is the association in fact and so similar in occurrence are the two minerals that the latter has been called white sodalite by the local collectors. Like the sodalite it is found in seams, and yields specimens as much as two centimeters in thickness; it is white, lusterless, and has the fracture of sodalite, and probably it originated from the alteration of the latter. Two specimens of it, received from two different collectors, were analyzed, with the following results:

	A.	B.
H_2O	13.12	13.30
SiO_2	38.90	39.24
Al_2O_3	33.98	33.16
CaO	.05	Trace
Na_2O	13.21	13.07
K_2O	1.01	.88
Cl	Trace	....
	100.27	99.65

The alumina carried a trace of iron, and a doubtful trace of manganese was also indicated; hardness, 4.5; fusible easily to a white enamel; soluble in hydrochloric acid and gelatinizing upon evaporation; fracture irregular, resembling that of the sodalite. In general, the mineral may be said to have the appearance of a slightly altered feldspar, minus the distinct cleavage.

These analyses left little doubt in my mind that I had a new mineral to deal with, and one belonging to the zeolite family. Such minerals are well known derivatives of the nephelite group, and thomsonite and natrolite have especially been often noted. In composition the new product differs distinctly from natrolite, but agrees in ratios approximately with thomsonite; forming, so far as chemical evidence alone goes, the soda end of a series passing through rauite up to ozarkite, the last named mineral being the nearest towards the lime end of the series. A comparison of the analyses of these elæolite derivatives is worth making, on account of its suggestiveness. The ozarkite was analyzed by Smith and Brush; the rauite, from Brevig, by Paykull.[1]

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[1] Ber. deutsch. chem. Gesell., VII, p. 1334.

	Ozarkite.	Rauite.	Hydro-nephelite.
H_2O	13.80	11.71	13.12
SiO_2	36.85	39.21	38.90
Al_2O_3	29.42	31.79	33.98
Fe_2O_3	1.55	.57	....
CaO	13.95	5.07	.05
Na_2O	3.91	11.55	13.21
K_2O	....	....	1.01
	99.48	99.90	100.27

Inasmuch, however, as massive minerals, and especially those which are produced by processes of alteration, are always subject to doubt, I requested Mr. Diller to assist me with a microscopic examination of the new substance. He very kindly acceded to my request, and I subjoin an abstract of his results. In his report on it he says:

"A section was carefully prepared so as to show both the sodalite and the white lusterless mineral associated with it in such a way as to reveal their relations. The accompanying figure illustrates a small portion of the section as seen under the microscope.

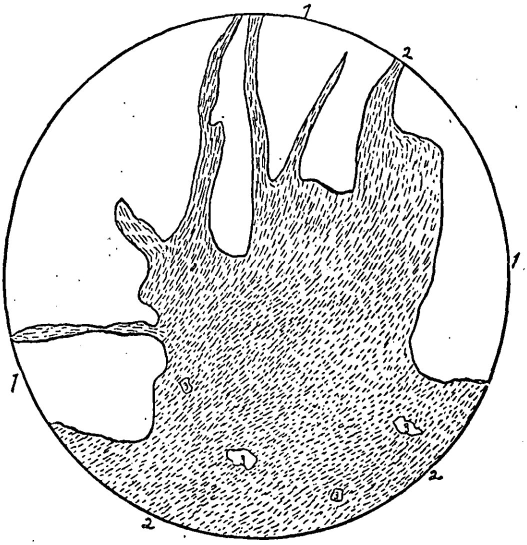

FIG. 2. Portion of thin section of hydronephelite.

"The unaltered sodalite (1) is quite irregular in form, so that the position of the section with reference to the crystallographic axes could not be determined. Although of a distinct, cobalt blue color in the small fragment, it appears colorless and transparent in the thin section, and under the microscope it is seen to contain numerous liquid inclusions. It is penetrated by many irregular fissures, which are enlarged in the process of alteration and filled with its clouded products. The extremely irregular line between the sodalite and its secondary products is well defined in transmitted light, but is even more distinct between crossed nicols from the fact that the sodalite, being isotropic, remains dark in all positions, while the other minerals are more or less brilliantly colored. The secondary products, which have clearly resulted from the zeolitization of the sodalite, are two in number. One of them forms very much the larger portion, probably nearly 90 per cent. of their total amount, and the other is embedded in the first in the form of distinct grains. Under the microscope in transmitted light the predominating mineral, which is doubtless a zeolite as shown by your analyses, is more or less deeply clouded, like decomposed feldspar. Between crossed nicols it breaks up into flaky grains, which vary considerably in the intensity of their color; some remain dark, others range through light and medium tints of red and yellow, according to the position of the section. The isotropic grains in converging light are proved to be distinctly uniaxial and positive, and the anisotropic ones, so far as can be determined, exhibit parallel extinction. It is evident therefore that the zeolite must be either quadratic or hexagonal in the system of its crystallization. Some of the grains show an indistinct striation approximately parallel to the vertical axis, but a distinct cleavage could not be discerned. In basal sections three sets of fractures could be rarely made out with sufficient distinctness to suggest that the mineral is probably hexagonal. The mode of its occurrence indicates clearly that it has resulted from the zeolitization of the sodalite, a phenomenon which has been observed in many rocks. The small grains of the other secondary mineral are so intermingled with the uniaxial zeolite as to indicate that both are derived from the sodalite. They are easily distinguished from the zeolite in which they are embedded. In transmitted light they are perfectly clear and transparent, with so high an index of refraction as to appear to rise above the surrounding mass. The grains are entirely without crystallographic boundaries, but are traversed by distinct cleavage lines. Between crossed nicols they are much more brilliantly colored than the associated zeolite, and if the section is rotated they become dark when the cleavage lines make a prominent angle (15°–33°) with the principal sections of the prisms. The mineral is certainly biaxial, and in all probability belongs to one of the two inclined systems of crystallization, but its definite determination is not practicable under the circumstances."

In view of the presence of an impurity in the new zeolite, Mr. Diller suggested a reanalysis of it to be made on carefully purified material. The purification, by means of Sonstadt's solution, he kindly undertook, determining at the same time the specific gravity of the mineral. The crude material gave him a sp. gr. of 2.263, while the zeolite was a little lighter and the embedded grains were a little heavier. After purification the coarsely powdered zeolite was carefully picked over under the microscope until Mr. Diller felt confident that the sum of all impurities could not exceed 1 per cent. The mineral, then dried at 100°, gave me the following analytical results:

H_2O	12.98
SiO_2	38.99
Al_2O_3	33.62
CaO	.07
Na_2O	13.07
K_2O	1.12
	99.85

These figures confirm the previous analyses and show that the impurity which vitiated them must have been small in amount and similar in composition to the new zeolite. The latter, I think, may be considered as fairly well established, and its formula may be written $Al_3(SiO_4)_3Na_2H,3H_2O$, which requires, water, 13.76; soda, 13.54; alumina, 33.41, and silica, 39.29. This composition and the manifest relations of the mineral to nephelite, the parent member of the group, naturally suggest for it the name *hydronephelite*, which seems to be both appropriate and descriptive. Chemically, as I have already observed, the species approximates to a soda thomsonite, but optically it appears to be quite different. This fact suggests the desirability of a careful microscopic re-examination of all the other massive zeolitic alterations of elæolite which, on analytical grounds, have been referred to the thomsonite series. Hydronephelite, indeed, is directly derived from sodalite, but the latter itself probably originated from elæolite; so that the new species may quite properly be considered along with the other zeolites which were previously mentioned. The fact that it contains more potassium than the sodalite is noteworthy and calls for an explanation which I am unfortunately not prepared to offer.

ALBITE AND LEPIDOMELANE.

The albite of Litchfield, which appears to be associated with other undetermined feldspars, is mostly in obscure masses. Occasionally a fragment is found with a translucent cleavage surface one or two centimeters broad. Such a specimen was partially analyzed, giving H_2O 0.52, SiO_2 66.39, Al_2O_3 19.69, K_2O 0.99, Na_2O 10.17. These figures serve only for complete identification of the species.

The lepidomelane exists abundantly in the elæolite rock, but mostly in small black scales. Sometimes tolerably large plates of it are found, black and brilliant, decidedly brittle, and apparently affected by alteration. An analysis gave the following results. The iron determinations were made by Mr. Riggs :

H_2O	4.62
F	None
TiO_2	None
SiO_2	32.09
Al_2O_3	18.52
Fe_2O_3	19.49
FeO	14.10
MnO	1.42
MgO	1.01
K_2O	8.12
Na_2O	1.55
	100.92

This analysis is noteworthy on account of the extremely low percentage of silica, which is approached, so far as I can ascertain, only in an analysis by Rammelsberg of a black mica from Brevig. The ratio between silicon and oxygen is nearly 1 to 5, which agrees with no known formula. My results make it extremely probable that the mica is a mixture and that it has undergone an alteration tending toward the ultimate development of some chloritic species. Still it deserves, as also do the feldspars of the locality, a more thorough examination.

DISCUSSION OF FORMULÆ.

In attempting to discuss the formulæ of cancrinite, sodalite, and hydronephelite, certain points should be carefully borne in mind. First, the three species must be considered, not independently, but relatively to one another, for all the evidence indicates for them a common origin. That origin is from the first member of the group, elæolite or nephelite, the empirical formula for which has been finally fixed by Rauff.[1] In partially rational form it may be written $Na_8Al_8(SiO_4)_7(SiO_3)_2$, ignoring the small replacement of sodium by potassium, which has been shown by synthetic investigations to be non-essential. Not only does the mode of occurrence and association of the minerals point to community of origin, but the same conclusion is emphasized by the experiments of Lemberg[2] upon the artificial alteration of silicates. When elæolite from Fredriksvärn was digested one hundred and eighty hours with a solution of sodium carbonate, a partial transformation into a *soda* cancrinite was effected, while a digestion of six months with a caustic soda solution containing sodium chloride gave a product identical in composition with sodalite. Many such experiments were tried by Lemberg, yielding a large class of similar results. His method of procedure probably did not give absolutely pure or definite compounds, and yet his researches

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[1] Zeitschr. Kryst. und Min., II, p. 445.

[2] Zeitschr. deutsch. geol. Gesell., XXXV, p. 557, 1883.

furnish evidence of great value in discussing the chemical structure of many minerals.

The taking up of sodium chloride by elæolite, both in the dry and in the wet way, has also been observed by Koch.[1] The easy alterability of elæolite, therefore, may be regarded as a point thoroughly established and to be taken into account in all discussion of it and its congeners.

If we compare the published analyses of cancrinite from different localities we shall find that they vary in two ways. First, there are variations which are probably due to admixtures of elæolite, such as I have shown to occur at Litchfield; and, secondly, the ratio between the lime and the carbonic acid ranges between rather wide limits. In the cancrinite from Miask, the two are about equivalent, while the Litchfield mineral contains only half enough calcium to saturate the carbonic acid. The lime and soda, however, vary reciprocally, so that when one is high the other is low; and, furthermore, the experiment quoted from Lemberg goes to show that a cancrinite may exist containing no lime whatever. If this conclusion be correct, then the carbonic acid of the mineral must be represented as linked with aluminum, a supposition which finds some justification in the existence of the rare species dawsonite. The function of water in cancrinite remains doubtful; if it be regarded as water of crystallization, the formula of the residue becomes less easy to write intelligibly; but, if it forms a part of the atomic structure, it is almost necessary to represent the carbonic acid as orthocarbonic in the group CO_4. This mode of consideration, as will appear later, leads to a simple general formula for cancrinite, covering all variations in composition except such as are due to impurity and correlating the mineral with the allied species sodalite and nosean. For the Litchfield mineral the following special formula may be written, giving the theoretical composition in the column below: $Al_8(SiO_4)_8(CO_4)_2CaNa_8H_6$.

	Found.	Calculated.
SiO_2	35.83 to 37.22	35.9
Al_2O_3	28.32 to 30.12	30.6
Na_2O	19.33 to 19.56	18.6
CaO	4.27 to 5.12	4.2
CO_2	6.22 to 6.96	6.6
H_2O	2.98 to 3.86	4.1
		100.0

In this case the water as found is slightly lower and the soda slightly higher than the calculated values, which is probably ascribable to the mutual replaceability of sodium and hydrogen.

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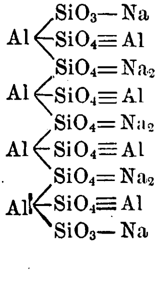
[1] Neues Jahrb., Beil. Bd. I, p. 143, 1881.

The formula commonly accepted for sodalite, and the one which is certainly the simplest, is that deduced by Bamberger[1] from his analysis of the mineral from Tiahuanuco. Written empirically, this formula is $Na_5Al_4(SiO_4)_4Cl$, which requires considerably less chlorine than has ordinarily been found in the species. In Bamberger's analysis, as finally corrected, he obtained 5.54 per cent. as against nearly 7 per cent. in Whitney's determinations. The difference he ascribes to silica in the chloride of silver, as weighed by other analysts; and yet in my own estimation every care was taken to eliminate such impurity, and my results confirm the older figures. Still, both figures have theoretical interest, as will be seen further on; and I am inclined to believe that the Bolivian mineral was more nearly typical than that from Litchfield. To the latter we may assign the empirical formula $Na_9Al_7(SiO_4)_7Cl_2$, which is directly derivable from the formula for nephelite and which agrees quite sharply with the analyses.

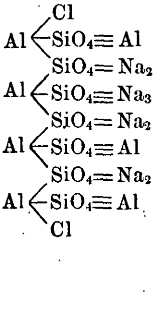
We now have three empirical formulæ ready for comparison side by side, as follows:

Nephelite	$Al_8(SiO_4)_7(SiO_3)_2Na_8$
Cancrinite (Litchfield)	$Al_8(SiO_4)_8(CO_4)_2CaNa_8H_6$
Sodalite (Litchfield)	$Al_7(SiO_4)_7Cl_2Na_9$

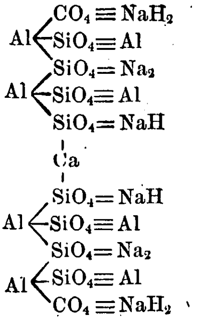
These may easily be put into structural form by an application of the principle suggested in a former paper,[2] that orthosilicates containing aluminum are to be represented as substitution derivatives of the normal salt $Al_4(SiO_4)_3$. The latter contains the fundamental nucleus $Al(SiO_4)_3$, which appears to be capable of a sort of polymerization, and which forms the basis of the subjoined symbols:



Nephelite.



Sodalite.



Cancrinite.

Now, although these formulæ fit the analyses and express a structural similiarity of type, two of them are capable of a further generalization. Remembering the reciprocal variations between soda and lime in different cancrinites and the fact that a soda cancrinite is quite pos-

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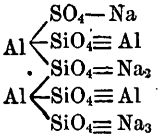
[1] Zeitschr. Kryst. und Min., V, p. 581.

[2] Topaz from Stoneham, Maine, Bull. U. S. Geol. Surv. No. 27.

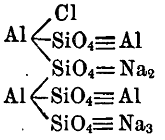
sible, we may write the following general formula for that species: $Al_4(SiO_4)_4CO_4Na_5H_3$; which requires

SiO_2	35.8
Al_2O_3	30.4
Na_2O (partly replaceable by CaO)	23.1
CO_2	6.6
H_2O	4.1

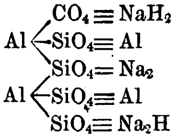
Comparing this with Bamberger's sodalite formula, and with the generally accepted formula for nosean, we have this remarkable series of structural expressions:



Nosean.

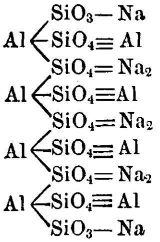


Sodalite.

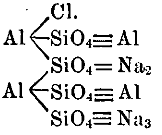


Cancrinite.

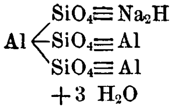
The formula of hauynite of course reduces to the same type, and so also, probably, does that of microsommite. Hydronephelite has a still simpler formula, which, however, includes three molecules of water of crystallization. It may be advantageously compared in series with its parent minerals, in which case we have the following set of structures:



Nephelite.



Sodalite.



Hydronephelite.

These formulæ express with decided clearness the natural order of transition from one species to another. The alteration of a mineral necessarily involves the passage from a less stable to a more stable condition; and in this instance we observe precisely that state of affairs. From a quite complex and therefore easily disturbed molecule, through an intermediate, simpler compound, we pass to one which is simplest of all, and hence presumably the most stable. I do not deny that such formulæ are subject to criticism and that possibly the advance of knowledge may brush them to one side; and yet I feel justified in claiming that they have some real value in the co-ordination of observed facts, and that, through their singular suggestiveness, they assist in the prosecution of research.

TURQUOISE FROM NEW MEXICO.

By F. W. Clarke and J. S. Diller.

At Los Cerillos, New Mexico, about twenty-two miles southwest of Santa Fé, are mines of turquoise which have been worked for centuries. The locality has been repeatedly described[1] from archæological and geological points of view; but, so far as we are able to ascertain, the turquoise itself has never been fully analyzed, nor has it been subjected to complete microscopic study. Having at our disposal a very full suite of specimens, collected during the summer of 1885 by Maj. J. W. Powell, Director of the United States Geological Survey, we have thought it desirable to investigate the subject more thoroughly, and to present our results in such a form as to render them readily comparable with the published data concerning turquoise from other localities.

The turquoise occurs embedded in its matrix, sometimes in nodules, oftener in seams or veins. It varies in color very widely, ranging from a pure sky blue through many shades of bluish green and apple green to dark greens which show no blue whatever. The dark green nodules often shade off to nearly white at the center, sometimes resembling in structure, as Blake has observed, certain varieties of malachite. Many of the specimens are seamed or streaked by limonite, which has been derived from accompanying pyrite; and the latter mineral occasionally is found, bright and unaltered, inclosed completely in masses of clear blue turquoise.

For analysis, three samples of turquoise were selected, representing, as nearly as possible, the most definite types of the mineral. They may be summarily described as follows:

A. Bright blue, faintly translucent in thin splinters.

B. Pale blue, with a slightly greenish cast, opaque and earthy in luster, and of sp. gr. 2.805. Blake gives the density from 2.426 to 2.651 for the green variety.

C. Dark green, opaque.

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[1] W. P. Blake, Am. Jour. Sci. (II), XXV, p. 227, 1858. J. S. Newberry, Report of the Exploring Expedition from Santa Fé to the Colorado, &c., 1859 (Macomb's Expedition). B. Silliman, jr., Am. Jour. Sci. (III), XXII, p. 67, 1881.

	A.	B.	C.
H_2O	19.80	19.60	18.49
Al_2O_3	39.53	36.88	37.88
Fe_2O_3	......	2.40	4.07
P_2O_5	31.96	32.86	28.63
CuO	6.30	7.51	6.56
SiO_2	1.15	.16	4.20
CaO	.13	.38	Undet.
	98.87	99.79	99.83

Analysis A is not quite complete, for enough material could not be obtained without the destruction of too valuable specimens. The silica in it was due to traces of admixed rock, from which the material could not well be perfectly freed. C, however, was free from rock, and the silica in it must be accounted for otherwise. Silliman reports the turquoise as containing 3.81 of copper, which corresponds to 4.78 of CuO, but he gives no other quantitative data.

In attempting to discuss these results, it will be well to compare them with three other published analyses of turquoise from different localities. First, we have the figures given by Church[1] for the well known variety from Persia; secondly, the analysis by G. E. Moore[2] of turquoise pseudomorphous after apatite, from Taylor's Ranch, Fresno County, California; and, thirdly, Nikolaieff's[3] data concerning the mineral from Karalinsk, in the Kirghiz Steppes. These analyses may be tabulated as follows:

	Persia.	California.	Karalinsk.
H_2O	19.34	19.98	18.60
Al_2O_3	40.19	35.98	35.79
Fe_2O_3	....	2.99	3.52
FeO	2.21	....	....
MnO	.36	....	....
CuO	5.27	7.80	7.67
P_2O_5	32.86	33.21	34.42
	100.23	99.96	100.00
Sp. gr	2.75	2.798, 2.815	....

These analyses, leaving temporarily out of account that of the dark green variety, agree well with one another in their atomic ratios. Divid-

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[1] Church, Chem. News, 10, p. 290; Dana's Syst. Min., p. 581.

[2] Zepharovich and Moore, Zeitsch. Kryst. und Min., 10, p. 240.

[3] In a paper by Kokscharoff, Neues Jahrb., 1886, I, Ref., 10.

ing the percentages by the proper molecular weights and treating the bases together, the following ratios appear:

	Total base.	P_2O_5.	H_2O.
New Mexico, A....	.468	.225	1.100
New Mexico, B....	.479	.231	1.089
Persia............	.492	.231	1.075
California........	.470	.234	1.110
Karalinsk.........	.470	.242	1.033

In each case the base stands to the acid in a ratio very slightly in excess of two to one, and that excess may fairly be accounted for upon the supposition that it represents a trifling admixture of limonite. The water is present in a proportion a little under that of five molecules to one of phosphoric acid, the variation here being due to differences in the percentages of copper. If we calculate the amount of phosphoric acid necessary to satisfy the alumina and then reckon the phosphate so obtained as requiring five molecules of water, we shall have left over a quantity of copper, acid, and water corresponding to a very simple formula, and the turquoise will appear as a variable mixture of the two following salts:

$$2\ Al_2O_3,\ P_2O_5,\ 5\ H_2O$$
$$2\ CuO,\ P_2O_5,\ 4\ H_2O$$

In the Californian turquoise the analytical results fit these formulæ quite sharply and give the ratio between the two compounds as approximately four to one. The first formula may be regarded as that of normal turquoise, and may be written in rational form, halved, as

$$Al_2HPO_4(OH)_4$$

The copper salt, to which the mineral owes its color, is to be considered merely as an impurity, a view which is emphasized by the analysis of the dark green turquoise C. In the latter case the same ratios apply, modified by the presence of silica, which is nearly sufficient to form with the copper a normal metasilicate, similar to if not identical with chrysocolla. This silicate, with whatever blue tinge of color it might have, affected by the yellow or brown of the iron present, probably gives the turquoise its green hue. It is exceedingly probable that the purity of tint in gem turquoise is due to the copper salt alone and that degradations of the color towards green are ascribable to admixture of salts of iron. It is noteworthy that of the three turquoises analyzed the bluest contains the lowest percentage of copper. This could hardly be the case were not the colors of the other samples modified by some impurities, and compounds of iron would naturally produce an effect in the observed direction.

Sections of the three varieties of turquoise were studied under the microscope and found to be of essentially the same character. Although deeply colored in the hand specimens, the thin sections appeared almost clear and transparent. Between crossed nicols the deep blue and green forms were seen to be composed of minute grains or short, thick fibers, but in the paler varieties the fibrous structure was more pronounced. The optical properties of both grains and fibers are the same throughout. They are all weakly doubly refracting, but have a rather high refractive index. The finely granular portions have a pale bluish aggregate polarization, less intense than that of chlorite, but when the mineral is distinctly fibrous it polarizes like some forms of serpentine, with light colors of the first order. The fibers are generally somewhat bent and interwoven, but lie approximately in the same direction. Each fiber becomes dark when parallel to the principal section of either of the crossed nicols, indicating that they must crystallize according to the quadratic, hexagonal, or rhombic system, instead of in one of the inclined systems, as was the case with the fibers studied by Bücking[1] in the turquoise of Fresno County, California.

A section was prepared of a distinct vein of pale green turquoise, which showed that the fibrous structure is directly across the vein perpendicularly to its walls. Small fissures, running into or across the veins, have the fibers of turquoise arranged perpendicularly along their sides, just as serpentine arranges itself along fissures in olivine. Sometimes the fissures are minute and curved; but the resulting arrangement does not simulate the radial fibrous or spherulitic structure described by Bücking[2] as found in the turquoise of California, Nevada, and elsewhere.

The perpendicular arrangement of the turquoise fibers along fissures crossing the vein indicates that the mineral may have been derived from the alteration of another substance with which the vein was formerly filled. We would suppose, of course, that the original vein material was itself a phosphate; and the only one after which turquoise is known to be pseudomorphous is apatite, a species which not infrequently occurs in veins. The opinion that the turquoise has resulted from such an alteration is favored by the presence of other alteration products, to be noted in considering the composition of the country rock in which the turquoise is found. It is also suggested by Hermann's analysis of blue Oriental turquoise, in which the equivalent of 3.41 per cent. of calcium phosphate was actually determined.[3]

The rock in which the veins of turquoise occur is described by Blake as "a granular porphyry, yellowish, gray, or white in color, porous and earthy in texture. It decomposes rapidly by weathering and very much resembles a sandstone." In the collection made by Major Powell there

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[1] See paper by Zepharovich and Moore, Zeitschr. Kryst. und Min., 10, p. 240; already cited.

[2] Zeitschr. Kryst. und Min., 2, p. 163.

[3] See Dana's Syst. Min., p. 581.

are several good examples of the rock penetrated by the turquoise. It is a fine grained, reddish, feldspathic rock, mostly fresher than that described by Blake, and it has a microgranitic aspect. It contains numerous particles of biotite and pyrite, with stainings of oxide of iron. The hand specimens look as though they had been crushed, and the fissures thus formed so filled as to produce irregular veins and nodules. The veins are small and mostly composed of turquoise, in which are embedded a few scales of biotite, particles of pyrite, and considerable quartz and oxide of iron. Scales of biotite are found abundantly in the iron stained cavities, as well as in the solid portions of the rock. Some specimens of rock, containing much pale blue turquoise of earthy texture, have been completely kaolinized, and a partial analysis of the kaolin gave the following results:

H_2O	12.88
SiO_2	52.38
$Al_2O_3+Fe_2O_3$	33.49
P_2O_5	None
MgO	1.17
CaO	Trace
	99.92

Although the mineral itself was white, the alumina from it was distinctly reddish with the iron.

Under the microscope the rock is seen to be composed chiefly of feldspar, with a considerable amount of biotite, epidote, pyrite, and limonite, and some amorphous substance. It is somewhat microgranitic in structure, and the irregular interlocking grains of feldspar vary in size from .01 to $.8^{mm}$ in diameter. Most of them are considerably kaolinized, so as to appear cloudy in ordinary light; but between crossed nicols the original outlines of the grains become more distinct. Their optical properties indicate that the feldspar is orthoclase, an opinion which is fully borne out by the subjoined analysis of the rock, which shows a remarkably large proportion of potash:

H_2O	3.28
SiO_2	56.68
Al_2O_3	16.62
Fe_2O_3	6.50
P_2O_5	.73
MgO	.79
CaO	.59
CuO	Trace, undet.
MnO	1.02
FeS_2	2.21
K_2O	11.18
Na_2O	1.03
	100.63

The porphyritic crystals are generally Carlsbad twins with irregular outlines. There are occasionally small grains of fresh, transparent plagioclase, which has evidently resulted from alteration.

The biotite of the rock occurs in noteworthy quantities, but is very unequally distributed. It is frequently aggregated in groups of scales and may be seen most abundantly in small cavities. It sometimes occurs intimately associated with the turquoise, but unlike the latter it is one of the primary minerals. The small quantity of quartz present is a secondary product, so intimately associated with turquoise as to suggest their genetic connection. Pyrite is scattered rather uniformly throughout the rock in small cubical crystals easily seen in the hand specimen. They are sometimes altered to limonite, but in other cases they have been completely replaced by pseudomorphs of epidote. The specimen of rock which was subjected to analysis probably contained an amount of pyrite rather greater than the average.

One of the most important constituents of the rock, because of its very close association with the turquoise, occurs in the form of bright yellow grains. They are not distinctly pleochroic, but have a high refractive index, with strong double refraction, and give brilliant aggregate polarization. The particles are usually very small and grouped together in irregular compound grains, so as to suggest nothing of crystallographic form. In several cases, however, elongated simple grains show inclined extinction, which indicates that the mineral must be either monoclinic or triclinic in crystallization. Judging not only from the properties enumerated, but also from the percentage of lime in the rock, this mineral is in all probability epidote. It is evidently connected genetically with the turquoise, for it is almost uniformly found upon the border of the latter and is most abundant in its neighborhood.

Concerning the origin of the turquoise bearing rock, it may be stated that Professors Newberry and Silliman, both of whom studied it in the field, regard it as eruptive and probably of Tertiary age. The occurrence of this veritable orthoclase rock in the West is of special interest from the fact disclosed by recent investigations that in many of the rocks previously described as trachytes the predominating feldspar is plagioclase.

The very small size of the veins and their limited distribution show that the turquoise is of local origin and emphasize the idea that it has resulted from the alteration of some other mineral. In addition to the evidence already cited to show that the turquoise has been derived from apatite, we have the fact that epidote, a lime bearing mineral, is present as a secondary product. The oxidation of pyrite may have had something to do with initiating the process of alteration and the alumina of the turquoise was probably derived from decomposing feldspar. The latter suggestion was made by Silliman, who also examined microscopic sections of the rock and reported apatite as present. No apatite, however, could be seen in the specimens examined by us. A search for it at the locality would certainly seem to be desirable.

THE GNEISS DUNYTE CONTACTS OF CORUNDUM HILL, NORTH CAROLINA, IN RELATION TO THE ORIGIN OF CORUNDUM.

BY THOMAS M. CHATARD.

The associations of corundum with the olivine or dunyte rocks of Western North Carolina and the adjacent portions of South Carolina and Georgia have been often described,[1] but, having had an opportunity during the summer of 1884 to visit a few of the typical localities and to collect specimens of the associated rocks, the results of my chemical examination of some of the latter are here given, as possibly affording some data for the solution of the problem of the origin of corundum.

The names given in this paper to the various rocks and minerals, unless analyses or authorities are given, must be considered as only approximately correct. By chlorite is meant all the varieties of green, foliated, hydrous, aluminous magnesian silicates met with in connection with dunyte, while the whole series of brown and yellow foliated minerals are called vermiculites. Under the heads of enstatite, talc, &c., are grouped a number of minerals of similar appearance, many of which may prove, on examination, to have compositions differing widely from that of the species under which they are placed.

In making the analyses, the silica, after being ignited over the blast lamp to constant weight, was treated with hydrofluoric acid and the residue deducted, while the alumina iron precipitate was, after ignition to constant weight, fused with sodic bisulphate, and silica, if present,

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[1] C. U. Shepard, Am. Jour. Sci. (III), IV, pp. 109, 175, 1872,
J. L. Smith, Am. Jour. Sci. (III), VI, p. 180, 1873.
F. A. Genth, Am. Phil. Soc., Sept. 19, 1873, July 17, 1874.
J. P. Cooke, Proc. Am. Acad., Vol. IX, pp. 48, 49, 1874.
C. W. Jenks, Quar. Jour. Geol. Soc., XXX, pp. 303-306, 1874.
W. C. Kerr, Geol. N. C., I, p. 64, Supplement.
C. D. Smith, Geol. N. C., I, Appendix D, pp. 91-97; II, pp. 42, 43, 1881.
R. W. Raymond, Trans. Am. Inst. Min. Eng., VII, pp. 83-90, 1878.
A. A. Julien, Proc. Bos. Soc. Nat. Hist., XXII, pp. 141-149, 1883.
M. E. Wadsworth, Mem. Mus. Comp. Zoöl., Lithological Studies, pp. 118, 119, 1884.
T. S. Hunt, Trans. Roy. Soc. Can., Vol. II, Sec. III, §§ 37, 38, 1884.
T. M. Chatard, Mineral Resources U. S., 1883-'84, pp. 714-720, U. S. Geol. Survey, Washington, 1885.

separated. Double precipitation was always employed and the precipitates were carefully tested.

THE LOCALITIES.

The principal southern mining localities for corundum are at Corundum Hill, Macon County, North Carolina, and at Laurel Creek, Georgia, 26 miles southeast of the former. Both are owned and worked by the Hampden Emery Company, under the direction of Dr. H. S. Lucas, to whom I am indebted for every desired facility and for a very warm and intelligent interest in my work.

The two localities are alike in respect to the occurrence of the corundum. In both, the mineral is found in chlorite and vermiculite lying between hornblende gneiss and altered dunyte. At Laurel Creek the open cut in which the corundum is mined runs east 10°–20° north, following the course of the veins, the mine being situated on the north bank of Laurel Creek, at the base of a high hill. On the south bank and in the bed of the creek, hornblende gneiss is the country rock, succeeded as we go northwardly by enstatite, talc, and allied minerals. The corundum first met with occurs in what is locally known as the "sand vein," which is composed of chlorite and vermiculite carrying more or less corundum, usually in small crystals and fragments. The chlorite in the upper portion of this vein was much disintegrated, the mass falling readily to pieces, allowing of the easy removal of the corundum, but at the time of my visit it was very compact and tough and of little value. The sand vein is succeeded by a so-called "horse" of steatite, on the other side of which is the vein of "block corundum." This is a vein of vermiculite containing masses of corundum sparingly mixed with chlorite and vermiculite and frequently of great size, several having been obtained of at least 5,000 pounds in weight. One mass which I saw must have weighed at least a ton. The north wall of the block vein is a smooth wall of "indurated talc" and steatite, which gradually passes into altered but still hard dunyte. Indeed, the difference between this place and Corundum Hill is in no respect more marked than in the greater hardness and toughness of the corundum bearing rocks and in the apparent concentration of the corundum into large masses with but little evidence of crystallization. At the westerly end of the cut is a vein of decomposed white material shown by analysis to be an altered soda lime feldspar. In this I did not find any corundum, but I was told that it was occasionally found in this rock.

The Corundum Hill mine is situated on a ridge which runs in the northeast and southwest direction characteristic of this section, the dunyte outcrops being on the crest, and apparently surrounded on all sides except towards the east by hornblende gneiss. On the east side mica schist[1] takes the place of the gneiss, and it is on the eastern side

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[1] Probably damourite schist; cf. Am. Acad., 1874, by F. A. Genth, "Damourite."

of the dunyte that the so-called "sand vein" is found. This is a vein-like mass of brown vermiculite in small scales containing an abundance of small crystals of corundum, which are usually brown in color and often broken into fragments. At the time of my visit the nearly perpendicular vein was about 6 feet wide and was worked by hydraulic washing through an open cut about 30 feet deep. The easterly wall of this vein is the mica schist very much decomposed, while on the western side we find enstatite, next vermiculite mixed with chlorite, then talc, which in turn gives place to nodules of more or less altered dunyte.

The specimens of corundum crystals for which this locality is so celebrated have all been found on the westerly side of the dunyte, and, so far as I have seen or could find out by inquiry from the owners and the miners, only on or near the lines of contact between the gneiss and the dunyte. The dunyte is sometimes, as stated by Julien in the paper cited, "interbedded with the hornblende gneiss in layers 1 to 6 meters in thickness. This was shown by a cross section of the beds on the north side of the dunyte deposit at the Jenks Mine (Corundum Hill), near Franklin, in Macon County. Although the dunyte is thus inclosed in or interbedded with the hornblende gneiss, the latter was never observed to be enveloped by the dunyte."

The origin of the dunyte, whether igneous or sedimentary, and, if the latter, whether mechanical or chemical, is a disputed question which has been ably discussed in the list of papers already given, and upon this point I am not able to give any further information of value. Leaving out the question of the origin of the dunyte, it appears very much like a dike or dike series, portions of which have been forced into the adjacent country rock without completely severing the connection with the main mass.

In its present condition it forms irregular spheroidal masses, sometimes several meters in diameter, most of which are much fractured and altered, the fracture seams being filled in with brown or yellow, clay-like, magnesian silicates, while the surface is also converted into a similar material which, when dry, has a strong tendency to peel off in semiconchoidal plates. In this form of alteration the mass of the nodule is still rather hard, but frequently the nodules are cased with talc, 10–20^{cm} in thickness and quite tough; when, however, this casing is pierced through, the interior is found to consist of a soft, yellow, ocherous material, into which a rod can be forced with comparative ease for a foot or more; towards the center of the nodule the material is often harder, being apparently less thoroughly decomposed.

The gneiss along the lines of contact is much decomposed, preserving its laminated structure but becoming a friable mass of reddish and brownish gray grains of quartz and scales of altered mica, with whitish nodules irregularly disseminated through it. Several contact sections from gneiss to dunyte were examined, and samples taken as the character of the formation seemed to change. Of these the results of the chemical examination of one series is given, as it is typical of them all, the variations in the others being due, apparently, only to differences in the relative proportions of the same general classes of minerals.

DESCRIPTION OF THE SECTIONS.

These sections were all taken in an open cut which starts from a point near the corundum mill and runs into the hill in a southeast direction. In this cut the exposures were clearest, the banks in most of the other cuts being more or less covered, either by caving or by débris piled against them in the course of the mining operations.

In going up the cut the walls were found to consist in most part of the material which I have called altered gneiss, with occasional masses of dunyte very much altered and showing the characteristic chloritic minerals. The cut at the upper end widens out immediately after passing through a belt of gneiss which crosses it with a northeast, southwest strike and a dip which is apparently eastward, but is nearly perpendicular. This rock can be traced northeast for some distance, but is then covered by mining débris, though Dr. Lucas informed me that it continued without an apparent break through that portion of the ground. Beyond the rock piles it can be traced to the main body in the higher part of the hill.

On the east side of this gneiss and on the north side of the cut we have the following sequence:

Section A.

A 1. Altered gneiss, becoming somewhat vermiculitic as it approaches A 2.
A 2. A narrow band of greenish chlorite.
A 3. A 6 inch seam of vermiculite.
A 4. Soft, yellow, magnesian clay.
A 5. A narrow seam of very impure chalcedony, stained red.
A 6. More yellow clay.
A 7. A rather hard casing, brownish yellow in color, inclosing
A 8. A large nodule of dunyte, much altered, with seams filled with soft clay and harder material of the same kind, while the comparatively hard brown yellow dunyte (A 8) has running through it small seams of
A 9. A mineral similar to enstatite.

Section B.

On the opposite side of the cut a section, B, starting from the same gneiss, shows —

B 1. Altered gneiss, like A 1.
B 2. About 2 feet (60^{cm}) of yellowish, micaceous, and quite rotten material.
B 3. About 30^{cm} of fine, scaly, brown vermiculite.
B 4. A band of foliated, compact, bright green chlorite stained bright red in places with ferric oxide or an iron clay.

B 5. Enstatite, gray in color and quite hard.
B 6. Yellow clay similar to A 6, and inclosing
B 7. Much altered but still rather hard dunyte, the casing on the other side being chlorite.

The corundum, when it occurs, is found in A 3 and B 3 and is much fractured.

Section C.

At about 10 meters northeast from A the Section C was made and gave the following series:

C 1. Altered gneiss, containing, distributed irregularly through it,
C 2. Harder nodules, very silicious; the gneiss gradually changing into
C 3. A scaly, brownish material, followed by
C 4. A soft, friable, yellowish white kaolin, intermixed with
C 5. A reddish brown, micaceous mineral, followed by
C 6. A seam of a small foliated, brownish yellow mineral which disintegrates easily, falling into small scales.
C 7. Vermiculite containing corundum. The specimen selected for examination was very typical and showed a mass of friable, yellowish brown vermiculite with a narrow seam of bright green chlorite dividing it into two nearly equal parts. The corundum is found on only one side of this chlorite seam, but is there in large proportion, some of the crystals being over 2^{cm} in length, the width of the corundum bearing streak being about 15^{cm}. The vermiculite containing the corundum was marked C 7 α; that on the other side of the chlorite, and which showed no corundum, C 7 β. This was followed by
C 8. A combination of vermiculite and actinolite.
C 9. Enstatite mixed with chlorite, forming a tough casing about 10^{cm} thick, inclosing a mass of altered dunyte with the yellow ochers and other characteristic decomposition products.

In giving the results of the examinations of these minerals it may be well to say that the rocks were always examined carefully with a strong lens and in most cases microscopically. The separations were made with Sonstadt's solution whenever practicable; but in the presence of the slimy, yellow, magnesian silicates this was often impossible, and hand picking was resorted to.

ANALYTICAL RESULTS.

C 1. Altered gneiss (?). A friable, sublaminated aggregate of scales of a micaceous mineral, in color from colorless to brownish and reddish yellow, with grains of quartz of similar shades of color and occasional small masses of a whitish, kaolin-like material (**C 2**). This rock has, as stated above, the same strike, dip, and structure as the adjacent unaltered gneiss and apparently passes into it.

C 2. Nodule in **C 1.** Structure finely granular, with larger grains of quartz disseminated through the mass, and a few small, yellowish scales on the fracture surfaces; rather friable; color brownish and yellowish white, with some small brown spots.

C 3. A friable aggregate of micaceous minerals, similar in structure and appearance to **C 1**, but the scales are smaller and more deeply colored in shades of brown and yellow, the grains of quartz are fewer and smaller, and the nodules **C 2** are absent.

	C 1.	C 2.	C 3.
Ignition	4.97	2.79	7.96
SiO_2	64.27	75.62	56.65
TiO_2	1.32	None	0.44
P_2O_5	0.05	None	Trace
Al_2O_3	16.75	12.52	21.60
Fe_2O_3	6.08	2.52	6.36
FeO	0.89	0.56	0.70
MnO	0.07	0.42	0.13
CaO	0.25	5.58	0.35
MgO	1.74	0.27	3.61
K_2O	3.09	None	1.98
Na_2O	0.89	None	0.59
	100.37	100.28	100.37

C 4. Soft, friable, fine granular, yellowish white, kaolin-like material, in lumps, with dark brown spots and streaks. Contains a very small proportion of fine grains of quartz.

C 5. The lumps of **C 4** are scattered through a seam of a small foliated mineral aggregated to a loosely coherent mass which breaks up when handled. The scales have a pearly luster and are apparently colorless or of a greenish tint, but are stained reddish brown by interlaminated ferric oxide whichcannot be separated from them. When heated the mineral exfoliates slightly, assuming a silvery luster and a purplish red color. Before ignition, decomposable by hot, concentrated hydrochloric acid.

C 6. A compact mass of translucent scales; color, yellow with shades of brown; apparently homogeneous, but altered; disintegrates easily; contains a little chromite (0.15 per cent.).

	C 4.	C 5.	C 6.
Ignition	13.70	12.63	9.46
SiO_2	45.71	37.96	52.59
Al_2O_3	35.49	22.53	5.26
Cr_2O_3	....	....	0.52
Fe_2O_3	1.82	11.12	2.33
FeO	0.60	0.30	0.69
MnO	0.06	0.12	0.12
CaO	0.30	None	0.33
MgO	1.61	15.46	28.53
Alkalies	0.34	Undet.	0.16
	99.63	100.12	99.99

C 7 α and **C 7 β**. This occurrence has been described above. The two vermiculites show but little difference in physical characteristics, both being fine, scaly, and of a pale brown yellow color. The thinnest scales have a pearly luster and are nearly transparent. **C 7 α** was carefully hand picked and showed no corundum under a magnifying glass, but the presence of it was shown not only in the course of the analysis, but also in the process of grinding, as the vermiculite when pure is quite soft and free from grit. The corundum is probably interlaminated with the vermiculite, as is often seen in specimens which are more broadly foliated;[1] moreover the corundum crystals, as separated from the gangue, are very much fractured and fall readily to pieces, often forming thin plates. **C 7 β** appears to be free from corundum. The analyses are given with total amount of water and are also calculated as being free from corundum and dried at 110°, the latter calculation showing that the two vermiculites are practically identical.

The narrow seam of chlorite separating these two was not examined chemically, as it did not differ apparently from the ordinary chlorites of this region. One chlorite (Analysis F, see page 56) has been examined on account of its peculiar appearance, but in most cases it was not deemed necessary:

	C 7 α.		C 7 β.	
	Air dried.	At 110°.	Air dried.	At 110°.
Corundum	8.87	....	None	....
H_2O at 110°	10.33	....	11.42	....
H_2O at red heat	9.47	11.60	10.05	11.34
SiO_2	31.01	38.02	32.97	37.22
Al_2O_3	15.14	18.56	17.88	20.19
Fe_2O_3	5.63	6.90	4.76	5.37
FeO	0.55	0.68	0.57	0.64
MnO	0.12	0.15	Trace	....
CaO	0.35	0.44	None	....
MgO	19.08	23.38	22.36	25.24
Alkalies	0.22	0.27	None	....
	100.77	100.00	100.01	100.00

C 8. A mass of a yellowish brown, small foliated mineral, through the central part of which runs an irregular seam of a fine, granular, grass green mineral intermixed with a small quantity of black magnetic grains and a large proportion of the vermiculite scales, which are, however, much smaller than those of the outer portions. As there were con-

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[1] Jenks, quoted by Cooke, Proc. Am. Acad., 1874, loc. cit.; Genth, Am. Phil. Soc., Sept. 19, 1873, section Chlorite.

siderable differences in the specific gravity of these minerals, they were separated by Thoulet's solution and marked **C 8** *α*, **C 8** *β*, and **C 8** *γ*.

C 8 *α*. Small rounded grains showing some octahedral faces; opaque; luster, submetallic; color, brownish black; streak, blackish brown; magnetic. Analysis corresponds to chromite intermixed with some magnetite, but FeO was not determined for itself, the whole of the Fe_2O_3 being calculated as such.

C 8 *β*. Finely granular, compact, the larger pieces showing under the magnifying glass a crystalline structure and longitudinal striations; translucent to subtransparent; luster, vitreous; color, grass green; streak, greenish white; sp. gr., 3.062. Analysis corresponds to actinolite.

	C 8 α.	C 8 β.
H_2O at 110°	....	0.04
H_2O at red heat	....	0.52
SiO_2	3.20	$\frac{2}{2}$55.23
TiO_2	0.36	None
P_2O_5	0.12	None
Cr_2O_3	45.94	0.19
Al_2O_3	2.51	$\frac{2}{2}$3.04
Fe_2O_3	....	1.88
FeO	42.90	2.51
(Ni,Co)O	....	Trace
MnO	0.84	0.26
CaO	None	13.36
MgO	3.91	22.31
Alkalies	....	0.58
	99.78	99.92

C 8 *γ*. Foliated, compact; folia generally small, not over 2^{mm} across; cleavage, basal, eminent; color, yellowish brown, the thinnest scales being almost colorless, with a greenish tint; luster, submetallic, somewhat greasy, the material having a great resemblance to the so-called "bronze powder." Easily decomposed by concentrated hydrochloric acid, the silicic acid separating in pearly scales. When heated gives off much water and exfoliates with considerable force, particles being projected several centimeters from the mass, which doubles its bulk and becomes reddish brown with a somewhat silvery luster. Examined microscopically by Mr. J. S. Diller, who reports "that it is biaxial and negative, but the angle between the optic axes, as seen in a cleavage plate split off parallel to the base, is uniformly small. Upon rotating the section, although the cross is plainly distorted into two hyperbolæ, they do not completely separate from each other." Sp. gr., 2.613 in water at 25.5°.

In the following water determinations the figures in brackets represent determinations by difference, the others being direct determinations.

	Per cent.	Per cent.	Per cent.	Per cent.	Average.
H_2O at 110°	3.87	3.81	3.72	3.72	3.78
H_2O at 130°	0.12	7.04			
H_2O at red heat (blast lamp)	(6.83)		(6.95)	(7.00)	(6.98)
Total H_2O as determined	10.82	(10.85)	10.67	10.72	10.76

Analyses Nos. 1 and 2 are the results obtained on the air dried mineral; No. 3, average of 1 and 2, and No. 4 the average calculated as dried at 110°.

	1.		2.	3.	4.
H_2O at 110°	3.78		(3.78)	3.78	....
H_2O at 130° and red heat	6.98		(6.98)	6.98	7.22
SiO_2	39.89		39.74	39.81	41.17
Al_2O_3	12.88	=18.82	19.04	12.99	13.43
Cr_2O_3	0.54			0.54	0.56
Fe_2O_3	5.29			5.29	5.47
FeO	0.11			0.11	0.11
MnO	0.05		0.05	0.05	0.05
CaO	0.14		0.13	0.14	0.14
MgO	24.88		24.78	24.83	25.68
K_2O	5.76		(5.76)	5.76	5.96
Na_2O	0.20		(0.20)	0.20	0.21
	100.50		100.46	100.48	100.00

No. 4 gives the atomic ratio:

$$\overset{\cdot\cdot}{\mathrm{Si}} : \overset{\cdot\cdot\cdot}{\text{Ɍ}} : \overset{\cdot}{\mathrm{R}} : \overset{\cdot}{\text{Ɍ}} : \overset{\cdot}{\text{Ħ}}$$

$$2.75 : \underbrace{1.03 : 1.29 : 0.14} : 0.80$$

$$2.75 : 2.46 : 0.80$$

$$7 : 6 : 2$$

As this mineral appears to be a very definite vermiculite, I have, in order to distinguish it from the others, given it the name lucasite, in honor of Dr. H. S. Lucas, of Corundum Hill, North Carolina, and the following table from Professor Cooke's paper[1] will show its relations to the other members of the group at 100°.

	$\overset{\cdot\cdot}{\mathrm{Si}}$:	$\underbrace{\overset{\cdot\cdot\cdot}{\cancel{\mathrm{R}}} : \overset{\cdot}{\mathrm{R}} : \overset{\cdot}{\cancel{\mathrm{R}}}}$	: $\cancel{\mathrm{H}}$.
Hallite	2.42 :	2.41	: 1.47 or 8 : 8 : 5
"Lerni"	2.54 :	2.50	: 1.30 or 2 : 2 : 1
Pelhamite	2.75 :	2.46	: 1.26 or 9 : 8 : 4
Culsageeite	2.50 :	2.66	: 1.23 or 2 : 2 : 1
"Millbury"	2.38 :	2.74	: 1.14 or 2 : 2 : 1
Jefferisite	2.56 :	2.53	: 1.17 or 9 : 9 : 4
Lucasite	2.75 :	2.46	: 0.80 or 7 : 6 : 2

C 9. Grayish white, asbestiform mass made up of fine fibers of a vitreous luster, aggregated to a somewhat woolly mass intermixed with a smaller proportion of bright green chlorite. The rock mass disintegrates easily, breaking down into a soft, woolly aggregate of fine needles, not folia. A hydrous enstatite. Sp. gr., 2.872.

H_2O	4.55
SiO_2	56.58
TiO_2	None
Cr_2O_3	0.24
Al_2O_3	1.74
Fe_2O_3	1.89
FeO	3.67
MnO	0.21
CaO	0.59
MgO	30.34
Alkalies	0.17
	99.98

The dunyte alteration following **C 9** was very much decomposed, being a friable, clay-like mass with needles of white, hydrous enstatite, like **C 9**, and small scales of another mineral which, however, could not be separated in a pure condition by means of Sonstadt's solution, as almost all the scales showed, when examined under the microscope, that they were interpenetrated by the needles. The examination of the decomposed dunyte of the **A** series will, however, show the character of these alteration products.

Of the following analyses, D is from the apparently least altered specimen of dunyte that I was able to find. It is granular, crystalline, the grains of olivine being subtranslucent, with a subvitreous luster and of an oil green color with grayish tints. The rock contains a little chromite.

Some of the specimens of dunyte, particularly the darker varieties, show an indistinct radiated structure, the radiations starting from points which are lighter in color than the rest of the specimen.

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[1] Cooke, Proc. Am. Acad., p. 461, 1875.

E is my old analysis of dunyte from the same locality, given in Dr. Genth's first paper on corundum, already cited.

	D.	E.
Chromite	0.56	....
H_2O	2.74	1.72
SiO_2	40.11	41.58
Cr_2O_3	0.18	....
Al_2O_3	0.88	0.14
Fe_2O_3	1.20	....
FeO	6.09	7.49
NiO (tr. Co and Mn)	....	0.34
CaO	....	0.11
MgO	48.58	49.28
	100.34	100.66

A 7 is the casing of the dunyte nodule of the **A** series. It is brownish yellow, granular, and, when dry, easily pulverized; but, some portions appearing harder than the rest, the specimen was crushed without grinding, the coarse powder shaken violently and then sifted through a fine sieve. The softer part was called **A 7** *α*, the harder **A 7** *β*, and it will be seen that the two are practically alike, the harder part containing much more chromite and being not quite so much decomposed.

	A 7 α.	A 7 β.
Chromite	0.17	2.45
Ignition	2.14	2.01
SiO_2	40.04	40.18
Al_2O_3	3.17	1.35
Fe_2O_3	12.15	9.88
MgO	42.97	43.84
	100.64	99.71

A 8. Altered dunyte, granular, compact, traversed by small seams carrying **A 9**. Luster, dull; color, pale yellowish brown. From interior of nodule.

A 9. Fine fibrous or small foliated, the folia being so arranged transversely in the seams of **A 8** as to present a fibrous appearance. Luster, pearly soft; color, colorless to white. Subtranslucent.

F. Chlorite; broad foliated, folia brittle, being probably somewhat altered. Color, dark bluish green; luster, submetallic. From Corundum Hill.

	A 8.	A 9.	F.
H_2O	1.54	4.32	12.71
SiO_2	40.25	56.39	35.88
Al_2O_3	0.96	2.31	20.90
Fe_2O_3	2.71	0.16	6.55
FeO	5.97	1.96	3.68
CaO	....	0.04	0.14
MgO	47.76	34.57	19.90
K_2O	....	....	0.19
	99.19	99.75	99.95

In comparing these analyses with reference to the mode of occurrence of the corundum and to the question of its probable origin, it must be remembered that we start from an aluminous rock, gneiss, on one side of the seam, and, passing through the series, reach as a final term a magnesian rock, dunyte. In following the series we should expect to find a progressive increase in the amount of magnesia and a gradual decrease in the amount of alumina. It will be observed that such is the case with the magnesia, while, roughly speaking, it is also true of the alumina. The ease with which magnesia, in the processes of rock alteration, may be dissolved and redeposited explains the regularity of its increase, while the high degree of insolubility of silicate of alumina and the presence of varying quantities of kaolin in the specimens **C 1** to **C 6** account for the irregularities in the alumina percentages. The members of the series **C 1** to **C 6**, though crystalline, are in nearly every case much decomposed and do not allow, generally, of proper separations. Enough has been done, however, to show that the entire series falls into three groups: aluminous silicates, alumino-magnesian silicates, and magnesian silicates. The list of constituents is practically the same for all, and it is only by considering the relative predominance of one or the other base that the distinction can be made. The middle term of the chemical series is also the middle term of the field series, and in it the corundum is found. All the gneiss dunyte contacts which I have seen or have information of give practically the same succession. Corundum is, however, only an accessory; frequently it is not found at all, and, when present, often in comparatively small quantities. It may therefore be considered as the result of a certain balance between the aluminous and the magnesian solutions, which have by their union produced the chlorites and the vermiculites.

The question of the origin of the dunyte, in so far as it has any reference to that of the corundum, can now be considered. Three modes of origin are supposable, chemical, sedimentary, and igneous. If a chemical origin be assigned to the dunyte (and gneiss), we could have a sequence of events something like the following: An aluminous silicate solution depositing the constituents of gneiss gradually becomes impregnated with a solution of magnesia either as silicate, or, more probably, a mixture of silicate and carbonate. The researches of Way[1] and those of Deville, Friedel and Sarrasin, and de Schulten[2] have shown that aluminous silicates and alkaline silicates can be made to combine, forming feldspars and other alkaline-aluminous silicates, and Way showed that the alkali could be replaced by lime.

Although much more work is required in this direction, still we are warranted in assuming that, if we can obtain solutions of aluminous silicates and of magnesian silicates and allow them to react upon each other under proper conditions, we shall obtain hydrous-alumino-magnesian silicates, or if iron be present, as is the case with dunyte, silicates belonging to the chlorite and vermiculite groups.

Under this assumption, the rock forming solution would cease depositing the constituents of gneiss, even of the more hornblendic varieties, and, instead, furnish chlorites and allied minerals, until, gradually becoming more and more magnesian, enstatites, talcs, and finally chrysolites would be the products. To account for the formation of corundum during this process we must suppose the presence of carbonate of magnesia along with the silicate, which would permit of the replacement, by magnesia, of a part of the alumina, which would be precipitated either as the hydrate or, under conditions as yet unknown, as corundum.

If instead of a chemical origin for the gneiss and dunyte we consider them as results of either a sedimentary or an igneous action, we shall find the reactions involved in the alterations of these rocks to be of the same character. In either case we should have gneiss in contact with dunyte. As soon as alteration of the gneiss begins, the feldspar kaolinizes and the mica is attacked, yielding solutions of alkaline salts which have the property of dissolving alumina, and this action is increased by the presence of carbonic acid, while even solutions of iron silicates and magnesian silicates have the same effect.[3]

As Roth observes, accurate and sufficient data are lacking for the proper consideration of such questions, but enough is known to be able to say that the alteration of gneiss or granite furnishes a solution of silicate of alumina. On the other hand, the mode of alteration of olivine has been studied,[4] and we know that both magnesia and silica are removed, the former in excess and therefore probably as carbonate,

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[1] Way quoted by Hunt, op. cit., § 97.

[2] Hunt, op. cit., §§ 98-99. Fouqué et Lévy, Synthèse des minéraux et des roches, pp. 32, 134, 161-164, Paris, 1882.

[3] Roth, Chem. Geol., Vol. I, pp. 112, 141-160, 305-334, Berlin, 1879.

[4] Roth, Chem. Geol., p. 113.

which, as such, is not an uncommon occurrence among these rocks. Iron would, of course, be dissolved in the same manner as magnesia.

Julien, in his paper already cited, says (page 147):

> The corundum itself is in all cases, both in the veins and in the particles found in the gabbro, a secondary or alteration product. All the phenomena of alteration, both in the veins and rock masses, absolutely require and can be simply explained by the introduction of a solution of soda and alumina into the fissures and interstices during the period of alteration and metamorphism. The combination of soda with silicates of alumina and iron, perhaps previously formed, has produced all the minerals of the vein series; while the precipitation of the alumina naturally ensued from the separation of its alkaline solvent. The question then presents itself of the evidence of the introduction of such a solution. This is found in the strata of hornblende gneiss, which everywhere surround the dunyte beds and are abundantly traversed all along the dunyte belt by huge veins of endogenous granite. Into these there has certainly been an introduction, by subterraneous thermal solutions, of soda and alumina, as shown both by the development of a long series of crystallized mineral silicates containing those bases with other elements, and, elsewhere, even by the precipitation of corundum itself (in association with muscovite, margarite, and albite) in a certain class of small veins in the gneiss of limited occurrence but of great interest.

Professor Julien's extended field experience among these rocks gives great weight to his opinion that corundum is a product of rock alteration. It is, indeed, difficult to see how a different opinion can be arrived at, if these rocks are studied in the field. In my own case, my field notes, written before I had an opportunity to see his valuable paper, indicate the same conclusion. Whether the solutions of soda and alumina must be heated in order to effect the production of these minerals is a question to which, at present, no definite answer can be given; but it would seem that the ordinary subaërial decay of these rocks should furnish the necessary solutions. The observations of Becker and the experiments of Barus[1] show that there is considerable doubt as to any production of heat as a result of the kaolinization of feldspar, and if such is the case with feldspar it is not likely that the alteration of any of the other mineral species present in these rocks would be attended by any marked rise in temperature. We must therefore conclude that the gneiss can furnish an alkaline solution of alumina and the dunyte a solution of magnesia without the production of heat and perhaps without its aid. Unless heat be absolutely necessary, either for the production of these solutions or for the formation of the contact minerals, we have no need for the introduction from a deeper source of a heated solution of alumina and soda, as the solutions furnished by the rocks at the contact should be sufficient for the purpose, and, by their meeting at the contact of the formations, give rise to the reactions stated above, namely, the production of chlorites and vermiculites, and, if the necessary conditions of proportion are reached, of alumina or corundum. That these conditions are often lacking is shown by the comparative

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[1] G. F. Becker, Geol. of Comstock Lode, Mon. U. S. Geol. Surv., Vol. III, Chaps. VII and IX.

rarity of the occurrences of corundum when the number of such chlorite bearing contacts is considered.

Among the miners chlorite or vermiculite is considered a "corundum sign," and they follow it as long as it holds out. The chlorite veins often extend for some distance into the dunyte, as should be expected when we consider the thoroughly fractured condition of the dunyte, with its consequent spheroidal alteration forms; but, in such cases, the connection with the contact can generally be traced. In the same manner the chlorite seams may extend into the gneiss.

It has already been said that the dunyte of Corundum Hill lies between hornblende gneiss and mica schist. The same can be said of the locality at Unionville, Chester County, Pennsylvania, and, to a certain extent, of that at Chester, Massachusetts.

Mr. W. W. Jefferis has kindly furnished me with much information about the former place, where the serpentine (probably resulting, as stated by Genth,[1] from the alteration of chrysolite rocks) lies between mica schist on the north and hornblende gneiss on the south. The great mass of corundum which was found at this place lay on the north side, in the serpentine, a short distance from the mica schist, and was accompanied by chlorite. "It was between well defined walls of serpentine" (Jefferis). At a point on the south side of the serpentine, at the contact with the hornblende gneiss, is "a digging 15 feet deep, which produced 500 pounds of extra fine, blue corundum, similar to the blue from Macon County, North Carolina. Culsageeite occurs here identical with the North Carolina specimens. Both the corundum and the culsageeite are so much like the Carolina mineral that it is difficult to tell them apart" (Jefferis).

The deposit at Chester, Mass., is a vein of emery situated nearly in the center of the Green Mountain chain.

It is included in the metamorphic series of rocks, here consisting of vast breadths of gneiss and mica slate, with considerable interpolations of talcose slate and serpentine. Strike, N. 20° E.-S. 20° W.; dip from vertical to 75°-80°, sometimes east, sometimes west. The immediate vicinity of the mine presents a succession of lengthened rocky swells, the longer axis of the elevations generally coinciding with the direction of the strata.

The emery vein traverses, in an unbroken line, the crests of two of these adjacent mountains, and is about 4 miles long and about 4 feet wide. It lies at the junction of the gneiss with the mica slate, just within the western edge of the gneiss, having throughout a layer of gneiss 4 to 10 feet in thickness for its eastern wall. Between this layer of gneiss and the mica slate is talcose slate about 20 feet thick at the south end and widening out at the northern end to nearly 200 feet.

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[1] Genth, Am. Jour. Sci. (II), XXXIII, p. 202, 1862.

The gneiss is highly hornblendic; where hornblende is rare, epidote is found. Quartz is very deficient and no corundum is found in the gneiss. The talcose slate carries soapstone, chlorite, talcose dolomite, &c., and contains, here and there, corundum. Quartz is very rare. In the vein are found corundum, magnetite, margarite, ripidolite, biotite, andestite, tourmaline, and titaniferous iron.[1]

Whether or not this locality can be placed with those already described is a question to which, not having visited the mine, I cannot give an answer. There are many points of similarity, but the presence of the thin wall of gneiss on the eastern side of the vein brings a difficulty into the consideration of the problem. The presence of magnetite must also be explained; and, as the action of lime is here evident, it may be that this occurrence must be placed with that of the Cullakenee or Buck Creek Mine, Clay County, North Carolina, where lime has also played a part, as shown by the presence of margarite, zoisite, and oligoclase, the last carrying corundum.

The action of lime brings us to the occurrences of corundum in crystallized limestone, of which the emery deposits of Asia Minor and the Greek Islands, studied by J. L. Smith,[2] are the most important. In his memoir he says:

> In every instance I have found the emery associated with the old limestones overlying mica slate, gneiss, &c. It is embedded either in the earth that covers the limestone or in the rock itself, and exists in masses from the size of a pea to that of several tons' weight, generally angular, sometimes rounded, and, when in the latter form, they do not appear to have become so by attrition. * * * The emery has been formed and consolidated in the limestone in which it is found and has not been detached from older rocks, as granite, gneiss, &c., and lodged in the limestone at the time of its formation. My reasons for so thinking are the following:
>
> (1) In no instance could the closest investigation of the older rocks of these localities that are below the limestone furnish the slightest indication of the existence of emery there; and, moreover, the masses of emery in the limestone never had fragments of another rock attached to them. A few thin layers of mica slate were found in the limestone, but they were not in contact with the emery, nor contained any traces of corundum.
>
> (2) The limestone immediately in contact with the emery differs almost invariably in color and composition from the mass of the rock; and at Kulat, where the marble forming the rock is remarkably pure, the part in contact with the emery is of a dark yellow color resembling spathic iron, and contains a large portion of alumina and oxide of iron. The thickness of this interposing coat between the emery and the marble is variable; but, what is certain, it passes gradually into white marble, so that their crystalline structures run into each other, showing that they are one and the same rock. * * * What we see is just what should be expected in ferruginous and aluminous minerals forming and separating themselves from a limestone not yet consolidated.

Other reasons are given to prove this point, and he gives a most instructive example of a nodule of emery surrounded by two concentric layers, the inner of chloritoid, a hydrous silicate of alumina and iron,

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[1] J. L. Smith, Am. Jour. Sci. (II), XLII, pp. 83-93, 1866.

[2] Am. Jour. Sci. (II), X, pp. 354-370, 1850; XI, pp. 53-66, 1851.

the outer of margarite, a hydrous silicate of alumina and lime. Finally he says:

> At some future time * * * it will doubtless be found that emery forms the geognostic mark of extensive calcareous formations in that part of the world, just as the flints do in the chalk of Europe.

CONCLUSION.

From the foregoing examples it would seem that we have three types of corundum occurrences:

(1) In chlorites and allied minerals, the result of contact alterations between aluminous-alkaline silicate rocks and magnesian silicate rocks.

(2) In soda-lime feldspars, mainly depending upon the same reactions as No. 1, but complicated by the action of lime.

(3) In crystallized limestone, represented by the emery occurrences and that at Vernon, Sussex County, N. J., described by W. P. Blake.[1] As to the character of the reactions producing this last class of occurrences, I am not at present able to say anything, and it will require a careful study of the relative influence of magnesia and lime, in this connection, before any hypothesis can be stated.[2]

In considering the second type the facts that the feldspar is always a soda-lime feldspar, that it is found in connection with occurrences of the first type, and that margarite and other lime minerals are found in association point to a modification of type No. 1 through the action of lime. If the "hornblende gneiss" of the Buck Creek or Cullakenee Mine proves to be diorite, as has been stated, then we may be able to form a simpler idea of the course of the reactions.

The mode of origin of the dunyte is readily seen to be foreign to that of the corundum, since the chemical reactions involved in the production of the latter are practically the same under each theory. If a chemical origin be assigned to the dunyte, then the corundum and chlorite would be formed posterior to the gneiss and anterior to the dunyte, or even vice versa. If either the mechanical sedimentary or the igneous theory be assumed, then the corundum is posterior to both gneiss and dunyte and contemporary with the chlorite (and vermiculite), the two being equally alteration products. On the whole, it would seem that an igneous origin for the dunyte offers the simplest explanations.

That the chlorite and the corundum are contemporaneous is made evident by the intimate manner in which the two have crystallized together. In general the plates of chlorite would seem to have attained considerable size before the corundum began to deposit and fill up the interstices, so that we have compact masses ranging all the way from almost pure corundum to almost pure chlorite. The "block corundum" of Laurel Creek is an example of the first class, while the "sand vein

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[1] Am. Jour. Sci. (II), XIII, p. 116, 1852; C. U. Shepard, Am. Jour. Sci. (III), IV, p. 179.

[2] J. L. Smith, Am. Jour. Sci. (III), VI, p. 182.

chlorite" of the same place shows the latter form. While perfectly formed crystals of pure corundum are not uncommon, we frequently find crystals with regular faces, but apparently formed in a solution having large numbers of small plates of chlorite or vermiculite floating in it, so that the corundum crystals carry many of the folia inclosed in them. If such a crystal, carrying vermiculite, is boiled in acid, the vermiculite is decomposed and more or less of the crystal disintegrates into corundum sand. Such crystals are found at Corundum Hill and specimens exist in the collection of the National Museum.

Whether or not the vermiculites are to be considered as resulting from the alteration of chlorites is a disputed point. Specimens are frequently found which show an apparent change from chlorite into vermiculite, the dark green folia of the one passing into the yellow brown of the other,[1] but in most cases it is difficult to resist the conclusion that the chlorite now found with the vermiculite is not the residue of a process which has converted the rest into vermiculite. Such specimens from Corundum Hill show the chlorite apparently perfectly fresh and the form of the mineral entirely distinct from that of the associated vermiculite, being usually much more broadly foliated. Moreover, we find seams containing but little chlorite, the corundum being surrounded by vermiculite, while, but a short distance away and under apparently like conditions of exposure and weathering, veins are found filled with chlorite almost free from vermiculite. In this connection the observations of Cooke[2] are very interesting, and from what we know at present the derivation of one from the other is very doubtful. As to the relation of the chlorites (including vermiculites) to corundum, it is possible that this mineral may, in the process of alteration, occasionally furnish them; still, so far as field experience teaches, these minerals are the original gangue of the corundum and are not derived from it. The valuable researches of Dr. Genth have shown that this mineral does alter, and, in so doing, produces many different mineral species; but whether any given mineral occurring with corundum is a result of the alteration of the latter must be determined for each case by the examination not only of the specimen but of its field surroundings also. Even when we have before us an apparently decided pseudomorph of some mineral after corundum it may prove to be only a case of envelopment, and this is particularly likely to be the case where the mineral in question is found free from corundum in the same vein or even the same locality. Both damourite and margarite are found enveloping corundum, the outlines of the mass closely imitating the form of the inclosed crystal, so as to be easily mistaken for a true pseudomorph, and yet both of these minerals occur with corundum in such a manner that it is hardly possible to conceive that they are derived from it. The same may be

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[1] Genth, op. cit., 1873, section "Jefferisite."

[2] Cooke, Proc. Am. Acad., Vol. IX, pp. 49-50, 1874.

said of the lime-soda feldspars, which, in general, present all the appearance of a gangue and not of an alteration product.

In concluding this paper it may be said that the information on this subject which has been gathered by different observers, while in the aggregate of considerable extent, is so far neither sufficient nor of a character to enable any one to speak with any great degree of confidence as to the mode of origin of this interesting mineral. Much more work, both in the field and in the laboratory is necessary; and, as a thorough investigation in this direction cannot fail to elucidate many points of great value to chemical geology, it is to be hoped that such work will be done. The value of corundum from the practical standpoint, the ease with which it can be recognized when occurring with other minerals, the great scientific importance of alumina, not only in its pure and crystallized condition, but also as a principal constituent of the earth crust, and therefore playing a part in almost all geognostic reactions, its varied and sometimes inexplicable chemical behavior, all tend to promise a rich return to the well equipped investigator.

A METHOD FOR THE SEPARATION AND ESTIMATION OF BORIC ACID, WITH AN ACCOUNT OF A CONVENIENT FORM OF APPARATUS FOR QUANTITATIVE DISTILLATIONS.

BY F. A. GOOCH.

In all successful methods for the estimation of boric acid, its comparative isolation is a necessary preliminary. Fortunately, the removal of nearly everything which interferes seriously with the proper execution of methods is not particularly arduous, but, of ordinarily occurring substances, two, silica and alumina—both very commonly associated with boric acid—are especially annoying in this regard. In the separation of alumina the trouble lies in the tendency of the precipitated hydrate to carry and retain boric acid,[1] so that the two cannot be parted by means of ammonia or ammonia salts; with silica, the difficulty is in removing it completely. The volatility of boric acid stands, of course, absolutely in the way of treating with acid and evaporating to dryness, and every chemist knows the vainness of attempting to precipitate silica by means of ammonia, ammonia salts, or zinc oxide in ammonia. In Stromeyer's method[2] the presence of silica is peculiarly harmful, since in passing to the condition of potassium fluosilicate this substance nearly quadruples its weight, and to free the potassium fluoborate from contaminating fluosilicate requires, according to Fresenius,[3] at least six treatments by solution in boiling water, the addition of ammonia, and evaporation to dryness. Wöhler[4] recommends evaporating the hydrochloric acid solution to dryness in a flask fitted to a condenser, collecting the distillate, reuniting the latter with the residue, and filtering from silica; and the operation is successful so far as the complete removal of silica is concerned, but the alumina, if present, is still in condition to give annoyance, and the other bases are yet to be separated.

Advantage has long been taken of the volatility of free boric acid with hydrofluoric acid or with alcohol to secure its removal from fixed substances, but so far as I know no attempt has been made heretofore to secure its complete volatilization and estimation in the distillate. The experiments which I proceed to describe are the result of an effort to accomplish this end.

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[1] Wöhler, Ann. Chem. und Pharm., CXLI, p. 268.

[2] Ann. Chem. und Pharm., C, p. 82.

[3] Quant. Chem. Anal., p. 424.

[4] Handbook of Mineral Analysis, under Datholite.

Aside from the difficulties in manipulation and in the construction of apparatus which the use of hydrofluoric acid would involve, this reagent is otherwise plainly inapplicable to the purpose in view, and of other agents with which boric acid is known to volatilize freely methyl alcohol seems to present the most desirable qualities. Methyl alcohol, ethyl alcohol, and water are effective in the order in which they are named. Thus to volatilize 1 grm. of boric acid—the equivalent, speaking roughly, of about 0.5 grm. of boric anhydride—two treatments with 10 $cm.^3$ of methyl alcohol and evaporation to dryness in each case were adequate; for the volatilization of 0.2 grm. of boric acid were required two treatments of 10 $cm.^3$ each of ethyl alcohol, succeeding an evaporation with 50 $cm.^3$ of the same alcohol; and the residue of five evaporations of water over 0.4 grm. of boric acid, taking in each case 50 $cm.^3$ of water, followed by ignition, weighed 0.08 grm., or one-fifth of the original weight. In the presence of water, methyl alcohol is not equally effective; amyl alcohol and sulphuric acid restrain its action similarly, doubtless by dilution simply, and hydrochloric acid seems to possess no advantage over water alone in developing the volatility of boric acid. As an example an experiment may serve in which a solution of 0.4 grm. of boric acid in 50 $cm.^3$ of water, after being heated three times successively with 25 $cm.^3$ of methyl alcohol until the boiling point rose in every case nearly to that of water, and then evaporated to dryness, left a large residue which disappeared with a single charge of 25 $cm.^3$ of methyl alcohol applied by itself.

From the residue of the evaporation of borax with hydrochloric, nitric, or acetic acid, methyl alcohol, as would naturally be predicted, volatilizes the boric acid freely, though the presence of foreign material acts to a certain degree protectively and tends to diminish the rapidity with which the alcohol would otherwise effect extraction and volatilization. In case, however, that acetic acid is used to break up the borate, the tendency of sodic acetate to lose acid and become alkaline simply by exposure to evaporation in its aqueous solution makes it necessary to insure the acidity of the residue of evaporation by adding a drop or two of acetic acid before repeating the treatment with methyl alcohol.

On the whole, methyl alcohol shows itself to be an excellent agent by which to secure the volatilization of boric acid.

To retain free boric acid, magnesium oxide naturally suggests itself. According to Marignac[1] it is effective, and, if in the course of analysis it may have been partly converted to the chloride, it is easily regenerated by the action of heat and moisture. Marignac, it will be remembered, makes use of magnesia mixture—the chlorides of ammonium and magnesium with free ammonia—to fix the boric acid, evaporating the solution to dryness, igniting, extracting with boiling water, filtering, and weighing the residue, while the filtrate is again treated as before to re-

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[1] Zeitschr. anal. Chem., I, p. 406.

cover traces of the borate which has yielded to the solvent action of the water. During the drying and ignition the magnesium chloride yields hydrochloric acid, and it would seem scarcely possible that the magnesium borate should fail to show some loss of boric acid when both hydrochloric acid and moisture exert their action. Further, the presence of ammonia during evaporation does not prevent the volatilization of boric acid,[1] and Marignac regards the addition of it from time to time as of doubtful use. So it appears natural to look for some loss under such conditions, and Marignac fully recognizes the fact that the apparent accuracy of his method is due to the balancing of errors, the inclusion of foreign matter by the magnesium borate and the deficiency of the magnesia when precipitated as ammonio-magnesium phosphate together compensating for the loss of boric acid by volatilization. To bring the matter to the test, the following experiments were made. In them and in all succeeding experiments the boric acid was weighed in solution, the standard of this having been fixed by dissolving in a known weight of water a known weight of fused boric anhydride prepared in a state of purity by frequent recrystallization. The magnesium oxide employed was made from the pure chloride by precipitating by ammonium carbonate and igniting, and was free from lime and alkalies and so far as could be determined was otherwise pure. The whole operation of each experiment was conducted in one vessel, so as to avoid transfers. In all cases a weighed platinum crucible of 100 cm.^{3} capacity received a weighed portion of magnesia, and after ignition and subsequent weighing the weighed solution of boric acid was introduced. In experiments (1) to (4) the magnesia was thoroughly stirred in the solution of boric acid, the evaporation carried at once to dryness, and the crucible and residue ignited and weighed; in experiments (5) to (8), the magnesia was dissolved, after the addition of the boric acid, in hydrochloric acid sufficient in amount to prevent the precipitation of magnesium hydrate on the subsequent addition of ammonia, ammonia introduced in considerable excess in (7) and (8), in distinct excess in (5) and (6), the whole evaporated and ignited, the residue moistened and again ignited, and this last treatment repeated until the residue ceased to yield vapor of hydrochloric acid when heated.

	B_2O_3 taken.	MgO taken.	$MgO+B_2O_3$ found.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(1)	0.1734	0.5005	0.6607	0.1602	0.0132 –
(2)	0.1804	0.4973	0.6660	0.1687	0.0117 –
(3)	0.1793	0.4949	0.6640	0.1691	0.0102 –
(4)	0.1794	0.4941	0.6627	0.1686	0.0108 –
(5)	0.1807	0.4984	0.6542	0.1558	0.0249 –
(6)	0.1789	0.4974	0.6687	0.1560	0.0229 –
(7)	0.1806	0.4944	0.6684	0.1740	0.0066 –
(8)	0.1789	0.4959	0.6672	0.1713	0.0076 –

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[1] Rose, Pogg. Ann., LXXX, p. 262.

From these results it appears plain that under the conditions of the experiments neither magnesia alone nor the magnesia mixture is efficient in fixing boric acid; but in experiments (7) and (8), in which ammonia was employed in large excess, the loss of boric acid is least; so that it would seem to be the case that though ammonia is not a perfect preventive of volatilization it does exert a restraining action on the boric acid. That the magnesia mixture should be incapable of retaining entirely the boric acid present is, as has been pointed out, not surprising; but that the loss should be so great is rather startling, and more than suggests that the errors of Marignac's process are seriously excessive. The failure of magnesium oxide to hold back boric acid under the conditions of the experiment must be due to a cause other than that which determines the loss during the evaporation and ignition of the magnesia mixture, and for this it is natural to turn to the insolubility of the oxide, a quality likely to oppose some difficulty in the way of establishing complete contact between the boric acid and the magnesia during a short exposure. Direct tests of this point showed distinctly that mixtures of boric acid in water and magnesia, when submitted at once to distillation, yielded boric acid to the distillate; but that, if the mixtures were permitted to stand some hours before distilling, the oxide passed to the semigelatinous condition of the hydrate and retained the boric acid so firmly that turmeric failed to show the presence of the latter in the distillate. It is plain, therefore, that with sufficient preliminary exposure magnesia might be relied upon to retain boric acid; but inasmuch as long and perhaps somewhat indefinite periods of waiting are objectionable in any analytical process, it was thought best to try the effect of substituting lime for magnesia. Experiments (9) to (12), conducted like the previous ones, excepting only the use of carefully prepared and ignited calcium oxide instead of magnesium oxide, were made with this end in view.

	B_2O_3 taken.	CaO taken.	$CaO+B_2O_3$ found.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(9)	0.1810	0.9737	1.1560	0.1823	0.0013+
(10)	0.1819	0.9750	1.1583	0.1833	0.0014+
(11)	0.1808	0.9922	1.1810	0.1818	0.0010+
(12)	0.1833	0.9715	1.1560	0.1845	0.0012+

These figures indicate sufficiently that there is no loss of boric acid by volatilization when its aqueous solution is evaporated in contact with calcium hydrate; but, inasmuch as the comparative solubility of the latter is the quality which makes it effective where magnesia is not, it seemed desirable to test the action of calcium hydrate in alcoholic solutions, in which it is very insoluble. The experiment showed that when the solution of boric acid in methyl or ethyl alcohol is put upon lime and distilled at once loss is apt to take place, and sometimes to a very considerable amount, but that a short period of digestion, with occasional stirring—from five to fifteen minutes—is sufficient to obviate danger of volatilization of boric acid.

It appears, therefore, that, free boric acid being easily volatilized by means of methyl alcohol and fixed completely by calcic hydrate, the separation of the acid from almost everything with which it occurs ordinarily and its estimation subsequently depend only upon the practicability of distilling it from its compounds in such company that it may be retained by lime and its amount determined by the increase in the weight of the latter. Unlike magnesium chloride, calcium chloride does not yield its chlorine readily under the action of heat and moisture naturally retained; so that hydrochloric acid must not be present with boric acid which is to be estimated in the manner described. Calcium nitrate and calcium acetate both yield the oxide without difficulty upon ignition, and nitric and acetic acids are suitable agents, therefore, for the liberation of boric acid previous to distillation.

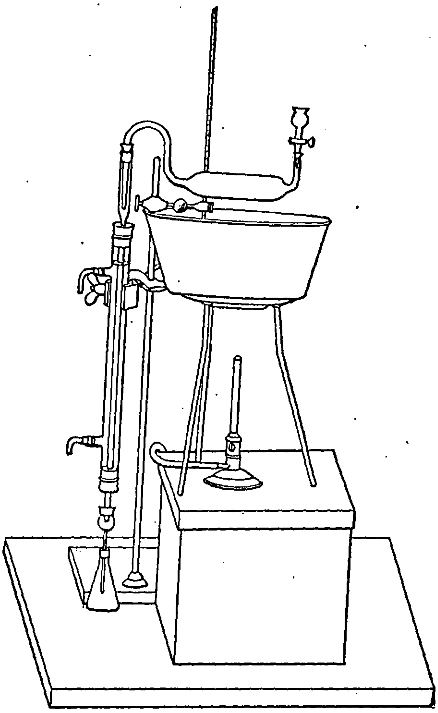

FIG. 3. Apparatus for determination of boric acid.

The actual distillation presented at first some difficulty, for the repeated, thorough, and rapid evaporation of a liquid charged with soluble or insoluble solid matter is apt to involve some mechanical transfer to the distillate of material which should remain in the residue; but the device of the following description solves the problem successfully.

The apparatus which is shown in the accompanying cut consists essentially of a retort, a condenser, and a bath for heating. For the last I have used a paraffine bath, as being, on the whole, the most convenient. The condenser is set vertically, to facilitate changing the level of the retort within the bath and to secure at the same time continual and thorough washing of the tube by its own condensations. The retort, somewhat like the well known drying tube of Liebig in general shape, is easily made of a pipette by bending the tube at one end to a right angle, at the other to a goose neck, as shown. To the former end is fitted, by a rubber stopper or section of tubing, a glass funnel tube provided with a stop cock; the end of the goose neck passes tightly through a rubber stopper in the upper end of the condensing tube. This is essentially the apparatus, but it is convenient to attach, to receive the distillate, a small Erlenmeyer flask, which moves with the condenser and is joined to it, in the manner indicated in the figure, by means of a thistle tube and a rubber stopper grooved to permit the free passage of air. In carrying out a distillation, the liquid to be distilled is introduced into the retort either by the funnel tube or previous to its insertion, the glass cock is closed, the water started through the condenser, and the retort lowered into the hot paraffine, care being taken to begin the operation with the retort not more than half full and so inclined that only the rear dips below the surface of the bath. If the precaution to heat the retort at the start in this manner be overlooked, it may sometimes happen that the sudden and violent expulsion of air through the liquid will carry portions of it bodily into the goose neck, and even into the condenser. With this point considered, the remainder of the operation presents no difficulty and requires little care.

The size of the retort may be suited, of course, to the particular case in hand, but for most purposes a 200 cm.^{3} pipette makes a retort of convenient dimensions, neither too large for the distillation of small charges nor too small to permit the treatment of 100 cm.^{3} of liquid comfortably. The tube of the goose neck should be wide enough to prevent the formation of bubbles in it; 0.7 cm. is a good measure for the interior diameter. It is of advantage to heat the bath to a point considerably above the temperature at which the liquid which is to be distilled boils — something between 130° C. and 140° C. does very well for water and is not too high for methyl alcohol — and under such circumstances, and when the retort is entirely submerged, it often happens that evaporation takes place with extreme rapidity from the surface of the liquid in perfect quiet without actual boiling.

With such an apparatus the following experiments were made. The boric acid was weighed, as before, in solution, and, to bring the condition of the experiment to that of an actual analysis, 1 grm. of pure sodium hydrate was added in solution, nitric acid or acetic acid to acidity and a little more, and the whole was introduced into the retort and distilled to dryness.

In those experiments in which nitric acid was employed, the methyl alcohol was introduced upon the residue thus dried in six successive portions of 10 cm.^{3} each and distilled to dryness; but in order to break up the residue of sodium nitrate, which by its insolubility might affect to some extent the protection of the boric acid from the action of the alcohol, 2 cm.^{3} of water were introduced and evaporated between the second and third and again between the fourth and fifth distillations.

When acetic acid was made use of to free the boric acid, the six distillations with methyl alcohol were made as before; but, sodium acetate being soluble in methyl alcohol, the intermediate treatments with water were unnecessary. With the fourth portion of methyl alcohol a few drops of acetic acid were added to preserve the acidity of the residue, which, as has been pointed out, tends to become alkaline under the treatment.

The residues of both processes of treatment were found to be free from boric acid by the exceedingly delicate test with turmeric, care being taken in the series of experiments in which nitric acid was used to oxidize nitrites by means of bromine (expelling the latter before making the test), and in the acetic acid series to acidify with hydrochloric acid sufficiently to counteract the tendency of the acetate by itself to brown the turmeric on evaporation.

The lime to retain the boric acid in the distillate was ignited in the crucible in which the evaporation of the distillate was to be made subsequently, and then transferred to the receiving flask attached to the condenser, so that the boric acid might be fixed during the distillation. To prevent the caking of the lime by the action of the alcohol, it was slaked with a little water before the distillation was begun.

In experiments (13) to (16) nitric acid was employed and in (17) to (20) acetic acid was used, with the precaution noted, to liberate the boric acid.

	B_2O_3 taken.	CaO taken.	B_2O_3+CaO found.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(13)	0.1738	0.9647	1.1392	0.1745	0.0007+
(14)	0.1806	0.9639	1.1456	0.1817	0.0011+
(15)	0.1779	0.9665	1.1450	0.1785	0.0006+
(16)	0.1824	0.9739	1.1587	0.1848	0.0024+
(17)	0.1806	1.4559	1.6371	0.1812	0.0006+
(18)	0.1812	0.9720	1.1543	0.1823	0.0011+
(19)	0.1788	0.9986	1.1781	0.1795	0.0007+
(20)	0.1813	0.9527	1.1358	0.1831	0.0018+

In experiments (13) to (16) the mean error amounts to 0.0012+ grm.; in experiments (17) to (20) the mean error is a little more than 0.0010+ grm. Throughout the entire series of experiments the tendency to yield figures slightly larger than the truth is manifest, but the error is quite within legitimate limits. The greatest care was taken to secure similarity of conditions under which the crucible and the lime were weighed before and after the evaporation and absorption of boric acid, and the weight after ignition was taken in every case after cooling over sulphuric acid during a definite period of ten minutes, in order to eliminate as far as possible the effect of atmospheric condensation upon the large surface of platinum. Ignitions were always finished over the blast lamp, and constancy of weights was secured.

The results indicate that both modes of treatment are on the whole equally satisfactory.

In the presence of chlorides, it is of course impossible to employ nitric acid to free the boric acid. Oxalic, citric, and tartaric acids also liberate hydrochloric acid to a considerable extent from alkaline chlorides. It was found, however, that when acetic acid was distilled over sodium and potassium chlorides only traces of hydrochloric acid passed into the distillate, and experiments (21) to (23) were made to determine whether these amounts are sufficient to vitiate the separation of boric acid from alkaline chlorides by distillation in presence of free acetic acid. The details of treatment were identical with those of experiments (17) to (20), excepting only the addition of 0.5 grm. of sodium chloride to each portion before distillation.

	B_2O_3 taken.	CaO taken.	B_2O_3+CaO found.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(21)	0.1834	0.9842	1.1675	0.1833	0.0001−
(22)	0.1831	0.9755	1.1593	0.1838	0.0007+
(23)	0.1761	0.9740	1.1523	0.1783	0.0022+

The mean error of these results is about 0.0009+ grm., and it is plain that the presence of sodium chloride does not materially change the conditions of the experiment. There seems, therefore, to be no reason why boric acid may not be separated by distillation from alkaline chlorides in presence of free acetic acid; but it was found that the presence of any considerable amount of potassium acetate is disadvantageous. Sodium acetate to a reasonable amount does not interfere with the favorable progress of the separation; but potassium acetate appears to require a much higher temperature for the expulsion of its water, and longer distillation.

When, therefore, chlorides are present in the salts from which boric acid is to be removed by distillation, the choice is open between two methods. The distillation may be made directly with an excess of acetic acid; or the hydrochloric acid may be first removed by means of silver nitrate and the distillation of the filtrate proceeded with at once or after precipitation of the excess of silver salt by means of sodium hydrate or carbonate, care being taken to acidify again sufficiently with nitric acid after the removal of the silver. Of these two modes of proceeding, I incline to the treatment with nitric acid and the removal of the chlorine by precipitation; and this method has been used with success by others as well as myself for some months in the analysis of waters carrying boric acid and natural borates.

The process in either modification is fairly accurate and easily executed and admits of very wide application. Insoluble compounds in which the boric acid is to be determined may be dissolved in nitric acid at once, or, if necessary, first fused with sodium carbonate; and, fortunately, nearly everything which is volatile in the subsequent treatment and capable of forming with lime compounds not easily decomposable by heat may be removed by known processes. The combination of fluorine, silica, and boric acid is perhaps most difficult to treat; but the precipitation and removal of the first as calcium fluoride from the aqueous solution of a fusion in alkaline carbonate may, it is believed, be effected with care, and the mode of procedure from that point is simple.

The number of distillations necessary depends, of course, upon the amount of boric acid treated. To remove 0.2 grm. of boric anhydride completely to the distillate, six charges of methyl alcohol, of 10 $cm.^3$ each, proved, as we have seen, to be ample.

The apparatus by the aid of which the distillation processes which have been described were carried out has found useful application in a number of other processes. In the determination of free and albuminoid ammonia in waters which can be boiled quietly with difficulty, in the methods of estimating hydrofluoric acid which involve the expulsion of silicon fluoride from a mixture of the fluoride with sulphuric acid and silica, in the separation of iodine from bromides and chlorides by distilling with ferric sulphate and sulphuric acid and of bromine from chlorides by means of permanganic acid, it has proved of value, and it will doubtless be found convenient in many analytical processes in which quantitative separations by the distillation of liquids liable to spatter or boil explosively are involved.

A METHOD FOR THE SEPARATION OF SODIUM AND POTASSIUM FROM LITHIUM BY THE ACTION OF AMYL ALCOHOL ON THE CHLORIDES, WITH SOME REFERENCE TO A SIMILAR SEPARATION OF THE SAME FROM MAGNESIUM AND CALCIUM.

By F. A. Gooch.

For the quantitative separation of lithium from sodium and potassium Mayer's method,[1] which is based upon the precipitation of lithium as the tribasic phosphate, and Rammelsberg's[2] mode of parting the chlorides by means of a mixture of anhydrous alcohol and ether in equal parts have been available.

The method of Mayer grew out of the older process of Berzelius,[3] which consisted essentially in treating the solution of the alkaline salts with phosphoric acid and sodium carbonate in excess, evaporating to dryness, and extracting with cold water. The result of a single analysis of the product thus obtained was the testimony upon which Berzelius rested the belief and statement that the salt was a double phosphate of lithium and sodium, which left upon ignition sodium and lithium pyrophosphates in equal molecules; and on this Berzelius based his process for the estimation of lithium. Rammelsberg,[4] however, showed later that it was a tribasic phosphate which was actually obtained, and from his experiments arrived at the conclusion that the proportions of soda and lithia were variable within wide limits, the amounts of the former varying in the special cases investigated from 7.84 per cent. to 28.38 per cent.; and the same thing in substance was reiterated subsequently[5] in an account of a repetition of the work suggested by the criticism of Mayer. Mayer,[6] however, was unable to prepare under any conditions the double phosphate of Rammelsberg, and obtained invariably, when the preparation had been washed with sufficient care, trilithium phosphate free from sodium; but the point was made that the phosphate is apt to be contaminated with lithium carbonate when sodium carbonate is employed to bring about alkalinity.

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[1] Ann. Chem. u. Pharm., XCVIII, p. 193.

[2] Pogg. Ann., LXVI, 79.

[3] Id., IV, 245.

[4] Loc. cit.

[5] Pogg. Ann., CII, 443.

[6] Loc. cit.

Mayer therefore modifies the method of Berzelius by substituting sodium hydrate for the carbonate, and, proceeding, evaporates to dryness, treats the dry mass with as much water as is needed to dissolve the soluble salts with the aid of heat, adds a drop or two of sodium hydrate if necessary to restore alkalinity, and then ammonia in volume equal to that of the water already added, sets aside at a gentle heat, filters only after twelve hours, and washes with a mixture of ammonia and water in equal parts. From the filtrate and first washings a small amount of the lithium phosphate is to be recovered by evaporation and the repetition of the former treatment. According to Mayer the precipitation of the phosphate may be effected with equal completeness by boiling the solution, prepared as before, instead of evaporating it; but the objection to this mode of proceeding is the tendency of the liquid carrying the precipitate to bump explosively. Careful washing, somewhat prolonged, is essential to secure the complete removal of salts of sodium and potassium, and it is remarked that the purity of the precipitate is shown by its failure to cake when strongly ignited.

This is the mode of proceeding by which Mayer separates lithium from sodium and potassium, isolating it as presumably pure trilithium phosphate and weighing it as the anhydrous salt. In dealing with mixtures of the chlorides in which the proportion of the lithium salt is relatively small, the removal of the greater part of sodium and potassium chlorides by a preliminary treatment with absolute alcohol is recommended. The following table comprises the results of Mayer's test analyses of lithium carbonate in the first seven, of lithium sulphate in the last two, recalculated with the use of the number 7 — the figure now generally accepted — as the atomic weight of lithium.

Li_3PO_4 equivalent to salt taken.	Li_3PO_4 found.	Error.
grm.	grm.	grm.
1.3586	1.3719	0.0133+
1.5172	1.5088	0.0084−
0.7519	0.7580	0.0061+
0.9561	0.9510	0.0051−
1.2651	1.2646	0.0005−
1.2197	1.2230	0.0033+
0.8991	0.9018	0.0027+
1.1325	1.1236	0.0089−
0.9715	0.9665	0.0050−

Fresenius[1] found on examining the method that several repetitions of the treatment by evaporation and extraction were required to complete the recovery of all lithium phosphate, and advised that the operation be continued until residual lithium phosphate fails to appear. The results of Fresenius's experiments with lithium carbonate, recalculated

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[1] Zeitschr. anal. Chem., I, p. 42.

with the use of the number 7 as the atomic weight of lithium, are given in the table appended.

Li_3PO_4 equivalent to salt taken.		Li_3PO_4 found.		Error.
		Dried at 100° C.	Ignited.	
grm.		grm.	grm.	grm.
0.7443	after two treatments	0.7243	......	0.0200 —
	" three "	0.7385	......	0.0058 —
	" four "	0.7433	......	0.0010 —
0.9820		0.9861	......	0.0041+
		......	0.9826	0.0006+
1.6341		1.6342	......	0.0001+
		......	1.6305	0.0036 —

Thus it will be seen that in the nine experiments of Mayer the error ranges from 0.0133+ grm. to 0.0089 — grm., and that of the determinations of Fresenius from 0.0001+grm. to 0.0041+grm. for the dried precipitate and from 0.0006+ grm. to 0.0036 — grm. for the ignited precipitate.

If the tendency of lithium carbonate to fall in company with the phosphate were not to assert itself during the evaporations of solutions of salts of lithium in presence of sodium hydrate and in contact with ordinary atmospheric air, it would surely be strange, and this point may be fairly set down as one of the weak ones of the method; but the gravest source of error, and that indicated most unmistakably throughout the whole history of the process — which has been recounted at some length for the purpose of emphasizing this very matter — is the impossibility of preparing the lithium phosphate in anything like a condition of freedom from other alkaline phosphates without a careful and prolonged washing, which is sure to result in loss of the lithium salt by solution. When it is remembered that according to Mayer's determinations trilithium phosphate requires for solution only 2,539 parts of water or 3,920 parts of a mixture of ammonia and water in equal portions, it is plain that the success of the method depends upon the ability of the analyst to wash to a condition of purity, and without loss of that which it is the purpose of the process to save, a precipitate peculiarly prone to retain foreign matter and soluble in the washing mixture in the proportion of 10 milligrams to every 40 cm.^{3} of the latter. Of course washings will never be entirely saturated, nor will the precipitate be as soluble at the beginning of the operation as at the end, when the precipitant no longer exerts an action which tends to lessen solubility; but in view of the difficulties which present themselves, it is sufficiently obvious that exact results obtained by Mayer's process owe their apparent accuracy to a fortuitous balance of errors. The difference of 0.0222 grm. between the extremes of Mayer's experimental results should not be surprising; and, at the best, the process is tedious and not entirely trustworthy, facts of which its author was not unmindful.

In Rammelsberg's method of separating lithium chloride from the chlorides of sodium and potassium the sources of error are, in brief, the solubility of sodium chloride and potassium chloride in the ether-alcohol mixture, the influence which the presence of small amounts of water exerts upon the solubility of these same salts, the difficulty of bringing the chlorides to the anhydrous condition without decomposing the lithium chloride to a greater or less extent, and the mechanical difficulties of transferring the fused or crusted chlorides to a suitable receptacle for digestion and agitation in the solvent, and of extracting perfectly the soluble constituents of closely compacted matter. Of the last two items nothing need be said in explanation beyond simply noting them. The third is particularily important, inasmuch as the tendency of lithium chloride, first noted I believe by Mayer, to exchange chlorine for oxygen when ignited in presence of water, results in the formation of lithium hydrate or, in contact with products of combustion, lithium carbonate, both of which are insoluble in the mixture of ether and alcohol and remain with the sodium and potassium chlorides. As to the effect of water in the mixture, an experiment of Mayer, in which it was found that 100 cm.^{3} of a mixture of alcohol of 96 per cent. and ether of 98 per cent. dissolved 0.1100 grm. of sodium chloride, is instructive. In regard to the solubility of the chlorides of sodium and potassium in the mixture of anhydrous ether and alcohol, Rammelsberg's statement that from 0.9770 grm. of pure, strongly heated sodium chloride with an undetermined amount of lithium chloride the mixture extracted 0.0130 grm. is unfortunately meaningless in the absence of information concerning the amount of solvent employed. J. Lawrence Smith[1] found, in making an examination of this matter, that 10 cm.^{3} of the anhydrous ether-alcohol mixture extracted from 0.5 grm. of sodium chloride 0.0005 grm. and from 0.5 grm. of potassium chloride 0.0003 grm. Smith's mode of applying the method is better than the original; for, by taking care not to heat the mixed salts above 100° C., the danger of decomposing the lithium chloride is diminished, and by treating the dried salts with the ether-alcohol mixture in the capsule in which it is heated and weighed (protecting it by a small inverted bell glass) the disadvantage of the transfer is avoided, but the danger is incurred that the mixed salts may not be thoroughly dried by heat so gentle. With this modification Smith obtained results which are rearranged in the following statement, and which do not throw a very favorable light upon the method:[2]

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[1] Am. Jour. Sci. (2), XVI, p. 56.

[2] Dr. Smith's language in the description of these experiments is somewhat ambiguous, but it is believed that these figures represent the meaning intended. After the presentation of the data of the first experiment given here with the correction of an obvious typographical error, it is said of the second and third experiments that "a similar mixture containing 18.10 per cent. of chloride of lithium furnished a residue of 17.65 per cent." and "a similar mixture containing 67.20 per cent. of chloride

NaCl taken. grm.	KCl taken. grm.	LiCl taken. grm.	Weight dissolved. grm.	Error. grm.
0.2000	0.2000	0.0080	0.0101	0.0021+
0.2000	0.2000	0.0884	0.0862	0.0022−
0.2000	0.2000	0.8195	0.8341	0.0146+

It is obvious, therefore, that neither the method of Rammelsberg nor that of Mayer may justly claim to be what a good process should be, accurate and rapid; and in the dilemma many chemists have been inclined to accept, with Bunsen,[1] the inherent disadvantage of an indirect process, and in a mixture of sodium and lithium chlorides calculate the percentage of each from the known weight of the mixture and its contents in chlorine, and in a mixture of the three chlorides calculate the percentage of each from the known weight of the mixture and the determined contents in chlorine and potassium. Here again, however, as in Rammelsberg's process, the difficulty of bringing the chlorides to a definite condition for weighing without decomposing the lithium chloride is an obstacle; and in case potassium is to be separated from large amounts of lithium by precipitation as potassio-platinic chloride, the concurrent precipitation of a similar salt of lithium, to which Jenzsch[2] has directed attention, may be the occasion of inexactness. So, the intrinsic unsatisfactoriness of indirect methods quite aside, it appears that in following Bunsen we have by no means all that is to be desired in an analytical method.

In looking about for better means for the separation of lithium from sodium and potassium, certain preliminary experiments on the behavior of the chlorides of these elements toward amyl alcohol gave very encouraging indications, and subsequent quantitative tests have borne out the hope that a successful method of separation might be based upon these relations.

In amyl alcohol the chlorides of sodium and potassium are highly insoluble, lithium chloride dissolves freely, and the attraction of amyl alcohol for water is so slight and its boiling point so far above 100° C. that the latter may be expelled without difficulty by the aid of gentle heating.

When amyl alcohol is poured into a solution of lithium chloride in water the liquid forms two layers, the aqueous solution of the salts at the bottom and the amyl alcohol now carrying a little water above. With the application of heat, the water evaporates slowly, then boils, and, passing through the alcohol, escapes, until toward the end of the operation the residual lithium chloride collects in a viscous globule and

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of lithium gave a residue of 68.40." I have taken this to mean that in all three experiments 0.2 grm. of sodium chloride and 0.2 grm. of potassium chloride were employed with the different proportions of lithium chloride indicated for each experiment. At all events, if this is not the meaning of the language made use of, it is difficult to see a definite value in the experiments.

[1] Ann. Chem. und Pharm., CXXII, p. 348.

[2] Pogg. Ann., CIV, p. 102.

finally dissolves, with the exception of a slight incrustation. If now the alcohol is cooled and a drop of strong hydrochloric acid is added and brought in contact with the deposit and the boiling repeated, the solution is complete. This deposit I take to be lithium hydrate, resulting from the decomposition of the chloride by the protracted action of water at a temperature near its boiling point. The small amount of water which is added in and with the hydrochloric acid seems to exert no unfavorable influence, but rather to be beneficial in hastening the solution of the residue by securing immediate and sufficient contact.

In hot amyl alcohol, lithium chloride appears to be a little more soluble than in the same reagent at ordinary temperatures, but the solubility under the latter condition only was determined. By boiling the solution until turbidity began to show, cooling, filtering, and then evaporating a known volume of the concentrated solution to dryness and weighing the residue after converting it to the sulphate, it was found that one part of lithium chloride was held dissolved in the cold in about fifteen parts of amyl alcohol, 10 cm.^{3} of the solution containing in the mean 0.66 grm. of the chloride.

When aqueous solutions of sodium chloride or potassium chloride are treated with amyl alcohol and boiled, the water disappears, as before, leaving first a globule of the concentrated solution and finally the crystalline salts. On continuing the boiling until a thermometer dipped in the liquid indicates the temperature at which the alcohol boils by itself, a slight additional precipitation, doubtless due to the expulsion of the water retained by the alcohol up to this point, takes place upon the walls of the containing vessel. The results of quantitative tests of the solubility of sodium and potassium chlorides are given in the following tables. The strengths of the solutions of sodium chloride and potassium chloride were determined by evaporating weighed portions in a platinum crucible and drying at a temperature considerably below the melting point of the salt, and weighing. The solution of lithium chloride was standardized by treating a weighed portion with sulphuric acid in excess, evaporating, igniting at red heat, and weighing. The standards were fixed by experiments (1) to (9).

	Weight of solution of NaCl taken.	Weight of NaCl found.	Weight of NaCl in 10 grm. of solution.	Mean.
	grm.	grm.	grm.	grm.
(1)	10.7110	0.1072	0.1001	0.1002
(2)	10.9419	0.1097	0.1003	
(3)	10.9325	0.1097	0.1003	

	Weight of solution of KaCl taken.	Weight of KaCl found.	Weight of KaCl in 10 grm. of solution.	Mean.
	grm.	grm.	grm.	grm.
(4)	9.3045	0.1744	0.1874	0.1872
(5)	10.7225	0.2006	0.1871	
(6)	11.1974	0.2096	0.1872	

	Weight of solution of LiCl taken.	Weight of Li_2SO_4 found.	Weight of LiCl in 10 grm. of solution.	Mean.
	grm.	grm.	grm.	grm.
(7)	10.9280	0.1635	0.1156	0.1154
(8)	11.1480	0.1665	0.1153	
(9)	10.8790	0.1626	0.1154	

To determine the solubility of sodium chloride and potassium chloride in amyl alcohol, portions of the test solutions were weighed out, evaporated to a convenient bulk in platinum crucibles of 100 cm.^{3} capacity, amyl alcohol was added, the water expelled by boiling, and the heating continued for some minutes after the thermometer in the liquid indicated 132° C., the boiling point of the alcohol employed. The liquid was then decanted with care and the residue dried at a temperature below its melting point and weighed. When the chlorides are precipitated in the manner described, the deposit generally adheres so closely and such particles as do remain loose settle so well that the supernatant liquid may be decanted to the end without appreciable transportation of the insoluble residue. For the sake of perfect security, however, in this part of the manipulation the decanted liquid was filtered under gentle pressure upon asbestus, with the aid of the device which I have previously described for such purposes,[1] and, after gentle heating, the increase in weight of the felt and the containing perforated crucible was added to the weight of the residual salt. In no case did this increase exceed a few tenths of a milligram and often could not be detected.

As a source of heat, a bath in which the sand of the sand bath is replaced by smooth asbestus board is a convenience, or a piece of asbestus board simply, about 30 cm. square, supported by a broad tripod and heated under the middle by a Bunsen burner, answers equally well to secure every gradation of heat without danger of igniting the evaporated alcohol.

As a control upon the results obtained by weighing the residue as described, the filtrate was evaporated in a large platinum crucible and the residue thus left gently heated and weighed. Though the evaporation be conducted with extreme care, the residue is almost sure to show some blackening, due to the carbonization of matter carried by the alcohol, which will not disappear entirely without the application of a degree of heat which the salts cannot bear without danger of volatilization. The weight of the residue from the amyl alcohol itself is small, one portion of 50 cm.^{3} yielding 0.0003 grm. and its mate 0.0007 grm., so that the data obtained by the evaporation of the filtered alcohol of the experiments, if not quite so trustworthy as the former testimony,

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[1] Proc. Am. Acad., Vol. XIII, p. 342.

may nevertheless serve the purpose of a very close control. Both sets of data are given in the following table:

	Weight of NaCl taken.	Total weight of NaCl found.	Weight found in residue.	Weight found in solution.	Volume of residual amyl alcohol.
	grm.	grm.	grm.	grm.	cm.^{3}
(10)	0.1062	0.1067	0.1043	0.0024	52
(11)	0.1043	0.1047	0.1024	0.0023	46
(12)	0.1024	0.1030	0.1003	0.0027	51
(13)	0.1003	0.1008	0.0983	0.0025	45

Reducing these figures to a common level to show the action of the same amount of amyl alcohol in every case we have:

	Loss of NaCl to 100 cm.^{3} of amyl alcohol.	Mean.	Weight of NaCl found in solution in 100 cm.^{3} of amyl alcohol.	Mean.
	grm.		grm.	
(10)	0.0037	grm. 0.0041	0.0046	grm. 0.0051
(11)	0.0041		0.0050	
(12)	0.0041		0.0053	
(13)	0.0044		0.0055	

	Weight of KCl taken.	Total weight of KCl found.	Weight found in residue.	Weight found in solution.	Volume of residual amyl alcohol.
	grm.	grm.	grm.	grm.	cm.^{3}
(14)	0.2091	0.2093	0.2074	0.0019	35
(15)	0.2074	0.2078	0.2059	0.0019	36
(16)	0.2059	0.2059	0.2040	0.0019	32
(17)	0.2040	0.2041	0.2015	0.0026	45

Derived from these figures we have:

	Loss of KCl to 100 cm.^{3} of amyl alcohol.	Mean.	Weight of KCl found in solution in 100 cm.^{3} of amyl alcohol.	Mean.
	grm.		grm.	
(14)	0.0049	grm. 0.0051	0.0054	grm. 0.0056
(15)	0.0041		0.0053	
(16)	0.0059		0.0059	
(17)	0.0056		0.0058	

From these figures it appears that the total weight of chloride found is always a little greater than that taken, the mean increase being 0.0005 grm. for sodium chloride and 0.0002 grm. for potassium chloride. It appears also that the residue left by the evaporation of the decanted and filtered amyl alcohol is greater than the loss put upon the chloride by the treatment: in the case of sodium chloride 0.0005 grm., in the mean, for every 50 cm.^{3} of amyl alcohol, which is about the quantity employed in the experiments; for potassic chloride 0.0002 grm., in the mean, for 40 cm.^{3} of amyl alcohol, which is approximately the quantity used in that case. It will be seen, therefore, that there exists for both salts an exact coincidence between the mean total excess found and the difference between the figures which indicate the solubility of the salts for the two methods of determination; and, taking this fact in conjunction with the results of the evaporation of amyl alcohol in blank (the mean residue being 0.0004 grm. for 40 cm.^{3}, and 0.0005 grm. for 50 cm.^{3}), it seems to be brought out pretty clearly that the former set of figures represents more exactly the solubility of the salts, though the difference between the two series is not great. Resting, then, upon the former determinations, the solubility of sodium chloride may be taken as 0.0041 grm. in every 100 cm.^{3} of anhydrous amyl alcohol, or one part in 30,000 parts by weight; and the solubility of potassium chloride, a little greater, is 0.0051 grm. to 100 cm.^{3} of amyl alcohol, or one part in 24,000 by weight.

The conditions under which the salts are acted upon are such as should insure the complete saturation of the solvent, and in this connection it is interesting to note that for the quantities of material employed the discrepancy between comparable figures never exceeds 0.0005 grm.

In experiments (10), (11), and (14), (15), the alcohol was decanted and filtered at once while hot; in (12), (13), and (16), (17), it was cooled to 30° C. before decanting; so it appears that the solubility of the salts is not influenced by changes of temperature within the range from 30° C. to 132° C.

Used simply to wash the precipitate, amyl alcohol cannot, of course, exert an effect at all comparable with that manifested in the experiments which have been described, but to know just what this action may be is important. Experiments (18) to (22) were undertaken, therefore, to elucidate this point.

Weighed amounts of the test solutions were evaporated nearly to saturation in small glass beakers, amyl alcohol added, and, as in the previous experiments, the whole heated until the salt had deposited and the residual alcohol had boiled quietly for some minutes at its ordinary boiling point, the liquid decanted, filtered under gentle pressure by means of a weighed perforated crucible and felt of asbestus, the filtrate measured, the residue dislodged with the aid of a rubbing-rod and transferred to the crucible and washed with anhydrous amyl alcohol, the washings being collected and measured. The crucible and contents were dried over a free flame turned low, so that the heat should not reach the melting point of the chlorides.

	Weight of NaCl taken.	Weight of NaCl found.	Weight of NaCl found, corrected for solubility in residual amyl alcohol.	Error of corrected weight of NaCl found.	Volume of residual amyl alcohol.	Volume of amyl alcohol in washings.
	grm.	grm.	grm.	grm.	cm.^{3}	cm.^{3}
(18)	0.0947	0.0937	0.0947	0.0000	24	44
(19)	0.1080	0.1074	0.1083	0.0002+	19	53

	Weight of KCl taken.	Weight of KCl found.	Weight of KCl found, corrected for solubility in residual amyl alcohol.	Error of corrected weight of KCl found.	Volume of residual amyl alcohol	Volume of amyl alcohol in washings.
	grm.	grm.	grm.	grm.	cm.^{3}	cm.^{3}
(20)	0.1846	0.1837	0.1847	0.0001+	20	60
(21)	0.1964	0.1946	0.1961	0.0003−	30	45
(22)	0.1857	0.1839	0.1854	0.0003−	30	60

These results show very plainly that the solvent effect of anhydrous amyl alcohol used for washing under the conditions described is trifling in the extreme, and may be neglected utterly providing the amount of the washing is not altogether disproportionate to the needs of the case.

We pass next to the consideration of the separation of the chlorides of sodium and potassium from lithium chloride. Weighed portions of the test solutions were concentrated and treated with amyl alcohol in the manner described until the precipitated salt was entirely free from water and the supernatant alcoholic solution of the lithium chloride boiled constantly at a point not far from that of the amyl alcohol employed. Then the liquid was cooled, a drop or two of strong hydrochloric acid was added in accordance with the evident suggestion of the preliminary experiments previously mentioned, and heat was again applied until the boiling had continued, as before, for some minutes at one point. The filtration, washing, drying, and weighing of the residue were effected as in experiments (18) to (22). In those of the experiments in which the lithium salt in solution was also determined, the end was accomplished by evaporating the filtrate and washings to dryness, treating the residue with sulphuric acid, and igniting and weighing as lithium sulphate. In the following table the weight of insoluble chloride actually found is given in one column, and this weight, corrected according to the data previously determined for the solubility of the chloride in the residual amyl alcohol, appears in the column adjoining. So also the weight is given of the lithium sulphate actually found, and an adjacent column contains the result of correcting this weight for the accompanying sodium or potassium sulphate, or both, upon the hypothesis that these salts are neutral sulphates after the ignition. In the case of quantities so minute the error which is introduced by such an assumption cannot be considerable, and in relation to this point Dittmar[1] maintains that comparatively large amounts of acid sodium or potassium sulphate may be reduced to the neutral salt by ignition simply. The figures of the column showing the weights of lithium chloride found are derived by calculation from the weights of lithium sulphate actually

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[1] Report on researches into the composition of ocean water, collected by H. M. S. Challenger during the years 1873-1876, p. 18.

found. The other headings of the table are sufficiently intelligible without further explanation.

	Weight of NaCl taken.	Weight of NaCl found.	Weight of NaCl found, corrected for solubility in amyl alcohol.	Error in weight of NaCl found.	Error in corrected weight of NaCl found.	Volume of amyl alcohol used. Residual.	Volume of amyl alcohol used. Total.
	grm.	grm.	grm.	grm.	grm.	cm.^{3}	cm.^{3}
(23)	0.1089	0.1092	0.1095	0.0003+	0.0006+	7	70
(24)	0.1084	0.1085	0.1090	0.0001+	0.0006+	12	80
(25)	0.1074	0.1067	0.1074	0.0007—	0.0000	18	90

	Weight of LiCl taken.	Weight of Li_2SO_4 found.	Weight of LiCl found.	Corrected weight of LiCl found.	Error in weight of LiCl found.	Error in corrected weight of LiCl found.
	grm.	grm.	grm.	grm.	grm.	grm.
(23)	0.1298	0.1682	0.1299	0.1296	0.0001+	0.0002—
(24)	0.1227	0.1592	0.1230	0.1225	0.0003+	0.0002—
(25)	0.0116	....	....	....	....	....

	Weight of KCl taken.	Weight of KCl found.	Weight of KCl found, corrected for solubility in amyl alcohol.	Error in weight of KCl found.	Error in corrected weight of KCl found.	Volume of amyl alcohol used. Residual.	Volume of amyl alcohol used. Total.
	grm.	grm.	grm.	grm.	grm.	cm.^{3}	cm.^{3}
(26)	0.2051	0.2036	0.2053	0.0015—	0.0002+	34	100
(27)	0.2022	0.2013	0.2032	0.0009—	0.0010+	37	100
(28)	0.2109	0.2096	0.2104	0.0013—	0.0005—	16	100
(29)	0.0984	0.0970	0.0980	0.0014—	0.0004—	20	90

	Weight of LiCl taken.	Weight of Li_2SO_4 found.	Weight of LiCl found.	Corrected weight of LiCl found.	Error in weight of LiCl found.	Error in corrected weight of LiCl found.
	grm.	grm.	grm.	grm.	grm.	grm.
(26)	0.1256	0.1638	0.1265	0.1248	0.0009+	0.0008—
(27)	0.1287	0.1677	0.1296	0.1277	0.0009+	0.0010—
(28)	0.0113	....	....	....	....	....
(29)	0.0113	....	....	....	....	....

	Weight of NaCl taken.	Weight of KCl taken.	Weight of NaCl+KCl found.	Corrected weight of NaCl+KCl found.	Volume of amyl alcohol used. Residual.	Volume of amyl alcohol used. Total.
	grm.	grm.	grm.	grm.	cm.^{3}	cm.^{3}
(30)	0.1053	0.1031	0.2064	0.2084	22	100
(31)	0.1051	0.0945	0.1988	0.2003	16	80

	Weight of LiCl taken.	Error in weight of NaCl + KCl found.	Error in corrected weight of NaCl + KCl found.
	grm.	grm.	grm.
(30)	0.0113	0.0020—	0.0000
(31)	0.0113	0.0008—	0.0007+

It will be noticed that in experiments (23), (24), (26), and (27) the corrected error in the weight of the insoluble chloride has a positive value, ranging from 0.0002+ grm. to 0.0010+ grm., with a mean of 0.0006+ grm.; and that in experiments (25), (28), (29), (30), and (31), the mean error is negative, amounting to less than 0.0001− grm., with a range from 0.0005− grm. to 0.0007+ grm.

The point of difference between these two series of experiments is the amount of lithium chloride introduced, only a tenth of that used in the former being employed in the latter. It is plain that, when we are dealing with the larger amount, a larger portion tends to remain behind with the insoluble chloride; and here again we meet, though to a degree comparatively harmless, the inclination of lithium chloride to yield chlorine and pass to the form of lithium hydrate. When the lithium chloride is present in small amount, as in the latter group of experiments, there can be little left undissolved; and the spectroscope confirms the evidence of the figures of analysis as to the perfectness of the separation by showing in such cases either no lithium at all or merely fugitive traces. If a single precipitation is sufficient to effect a satisfactory separation of the insoluble chlorides from small amounts of lithium chloride, it is natural to suppose that a repetition of the precipitation would be beneficial in treating larger quantities of lithium chloride.

Experiments (32) to (37) illustrate the effect of a double precipitation. The chlorides were brought to filtration as before, the liquid was decanted as completely as possible, the precipitate washed slightly by decantation and redissolved in a little water, and the round of boiling, filtering, drying, and weighing carried to the end as before, care being taken to repeat the treatment with a drop of hydrochloric acid during the process of boiling. The two portions of residual amyl alcohol were measured apart, as well as the washings.

	Weight of NaCl taken.	Weight of NaCl found	Corrected weight of NaCl found.	Error in weight of NaCl found.	Error in corrected weight of NaCl found.	Volume of amyl alcohol used. Residual. I.	II.	Total.
	grm.	grm.	grm.	grm.	grm.	cm.^{3}	cm.^{3}	cm.^{3}
(32)	0.1166	0.1163	0.1169	0.0003−	0.0003+	8	8	150
(33)	0.1139	0.1127	0.1132	0.0012−	0.0007−	5	7	150

	Weight of LiCl taken.	Weight of Li_2SO_4 found.	Weight of LiCl found.	Corrected weight of LiCl found.	Error in weight of LiCl found.	Error in corrected weight of LiCl found.
	grm.	grm.	grm.	grm.	grm.	grm.
(32)	0.1287	0.1662	0.1284	0.1280	0.0003−	0.0007−
(33)	0.1347	0.1759	0.1359	0.1353	0.0012+	0.0006+

	Weight of KCl taken.	Weight of KCl found.	Corrected weight of KCl found.	Error in weight of KCl found.	Error in corrected weight of KCl found.	Volume of amyl alcohol used. Residual. I.	II.	Total.
	grm.	grm.	grm.	grm.	grm.	cm.^{3}	cm.^{3}	cm.^{3}
(34)	0.1155	0.1142	0.1152	0.0013−	0.0003−	10	10	100
(35)	0.1034	0.1017	0.1028	0.0017−	0.0007−	10	12	200
(36)	0.1914	0.1905	0.1912	0.0009−	0.0002−	3	11	90
(37)	0.1953	0.1939	0.1950	0.0014−	0.0003−	4	18	110

	Weight of LiCl taken.	Weight of Li_2SO_4 found.	Weight of LiCl found.	Corrected weight of LiCl found.	Error in weight of LiCl found.	Error in corrected weight of LiCl found.
	grm.	grm.	grm.	grm.	grm.	grm.
(34)	0.1125	0.1475	0.1139	0.1128	0.0014+	0.0003+
(35)	0.1251	0.1649	0.1274	0.1162	0.0023+	0.0011+
(36)	0.1263	......	......	......	....	....
(37)	0.1282	......	......	......	....	....

Thus it appears that, in the separation of the insoluble chlorides from the larger amounts of lithium chloride, the residue of two precipitations is substantially free from lithium.

For the sake of bringing the data in hand more directly into comparison, the corrected errors of the preceding determinations are tabulated again in the following statement:

No. of experiment.	Chloride.	Corrected error of insoluble chloride—			Error in corrected weight of LiCl.	Approximate mean error of LiCl.
		Precipitated once from about 0.13 grm. of LiCl.	Precipitated once from about 0.013 grm. of LiCl.	Precipitated twice from about 0.13 grm. of LiCl.		
		Grm.	*Grm.*	*Grm.*	*Grm.*	*Grm.*
(23)	NaCl	0.0006+	....	....	0.0002−	0.0005−
(24)	"	0.0006+	....	....	0.0002−	
(26)	KCl	0.0002+	....	....	0.0008−	
(27)	"	0.0010+	....	....	0.0010−	
(25)	NaCl	....	0.0000	....	....	
(28)	KCl	....	0.0005−	....	....	
(29)	"	....	0.0004−	....	....	
(30)	NaCl+KCl	....	0.0000	....	....	
(31)	" "	....	0.0007+	....	....	
(32)	NaCl	....	....	0.0003+	0.0007−	0.0003+
(33)	"	....	....	0.0007−	0.0006+	
(34)	KCl	....	....	0.0003−	0.0003+	
(35)	"	....	....	0.0007−	0.0011+	
(36)	"	....	....	0.0002−	....	
(37)	"	....	....	0.0003−	....	
	Approx. mean.	0.0006+	0.00004−	0.0003−		

Few processes in analytical chemistry are capable of yielding results more exact than these. The separation of from 0.1 grm. to 0.2 grm. of sodium or potassium chloride from a tenth of its own weight of lithium chloride is practically perfect in one operation, and from its own weight of lithium chloride the parting may be effected satisfactorily by two precipitations.

The points to be observed in executing the method may be recapitulated as follows:

To the concentrated solution of the chlorides, amyl alcohol is added and heat is applied, gently at first to avoid danger of bumping, until the water disappearing from solution and the point of ebullition rising and becoming constant for some minutes at a temperature which is approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited and lithium chloride is dehydrated and taken into solution. At this stage in the operation the liquid is cooled and a drop or two of strong hydrochloric acid is added to reconvert traces of lithium hydrate in the deposit, and the boiling is continued until the alcohol is again free from water. If the amount of lithium chloride present is small it will now be found in solution, and the chlorides of sodium and potassium will be in the residue, excepting the traces, for which correction will be made subsequently. If, however, the weight of lithium chloride present exceeds ten or twenty milligrams, it is advisable at this point, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the residue, wash the latter a little with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling again in amyl alcohol. For washing, amyl alcohol previously dehydrated by boiling is to be used and the filtrates are to be measured apart from the washings. In filtering it is best to make use of the perforated crucible and asbestus felt and apply gentle pressure. The crucible and residue are ready for the balance after drying for a few minutes directly over a flame turned low. The weight of insoluble chlorides actually obtained in this manner is to be corrected by the addition of 0.00041 grm. for every 10 $cm.^3$ of amyl alcohol in the filtrate, exclusive of washings, if the insoluble salt is entirely sodium chloride, 0.00051 grm. for every 10 $cm.^3$ if potassium chloride constitutes the residue, and, if both sodium and potassium chloride are present, 0.00092 grm.; but, as in the experiments described, the entire correction may in any case be kept within narrow limits, if due care be given to the reduction of the volume of residual alcohol before filtration. The filtrate and washings are evaporated to dryness, treated with sulphuric acid, the excess of the latter is driven off, and the residue ignited to fusion and weighed. From the weight thus found the subtraction of 0.00050 grm. is to be made if sodium chloride constitutes the precipitate, 0.00059 grm. if potassium chloride alone is present in the residue, and 0.00109 if both of these chlorides are present, for every 10 $cm.^3$ of filtrate, exclusive of washings.

Amyl alcohol is not costly, the manipulations of the process are easy, and the only objectionable feature—the development of the fumes of amyl alcohol—is one which is insignificant when good ventilation is available.

The process has been used for some months frequently and successfully, by others as well as myself, for the estimation of lithium in waters and minerals.

In this connection it seems best to include the record of certain experiments looking to the separation of the chlorides of sodium and potassium from the chlorides of magnesium and calcium. The behavior of magnesium chloride toward amyl alcohol is of interest, both with reference to the problem of separating sodium and potassium from lithium and magnesium when the latter are associated and as concerns the parting of the alkalies from magnesium alone — a matter which is by no means perfectly simple — and experiments (38) to (41) touch upon this topic.

The chlorides of sodium and potassium were weighed, as before, in solution; the magnesium chloride was obtained by dissolving in hydrochloric acid the oxide specially prepared and weighed as such. The process of treatment was identical with that just described for the separation of the chlorides of potassium and sodium from lithium chloride.

	Weight of NaCl taken.	Weight of KCl taken.	Weight of NaCl+KCl found.	Corrected weight of NaCl+KCl found.	Volume of amyl alcohol used. Residual. I.	Volume of amyl alcohol used. Residual. II.	Volume of amyl alcohol used. Total.
	grm.	grm.	grm.	grm.	cm.^{3}	cm.^{3}	cm.^{3}
(38)	0.1030	0.1064	0.2079	0.2100	23	..	120
(39)	0.0967	0.1024	0.1976	0.2006	33	..	100
(40)	0.1030	0.1073	0.2071	0.2093	13	11	100
(41)	0.1053	0.1093	0.2114	0.2142	12	18	100

	Weight of MgO taken.	Error in weight of NaCl+KCl found.	Error in corrected weight of NaCl+KCl found.
	grm.	grm.	grm.
(38)	0.1000	0.0015—	0.0006+
(39)	0.1000	0.0015—	0.0015+
(40)	0.1000	0.0032—	0.0010—
(41)	0.1000	0.0032—	0.0004—

The residues of experiments (38) and (39), in which the separation was made by a single precipitation, carried traces of magnesia; those of (40) and (41), in which two precipitations were introduced, were found to contain in the one case no magnesia and in the other an unweighable trace. These results point out a method by which the chlorides of sodium and potassium may be obtained free from magnesia, while the small amounts of the former which pass into solution with the magnesium chloride are capable of accurate estimation; and there seems to be no reason why the separation of these alkaline chlorides from magnesium chloride and lithium chloride occurring together should not be effected in one operation, and the parting of the latter salts brought about by the familiar method of precipitating the magnesium in the cold as ammonium-magnesium phosphate.

Experiments (42) to (47), upon the separation of sodium and potassium from calcium by the action of amyl alcohol on the chlorides, yielded the figures of the following table. The mode of treatment was identical with that of the experiments with magnesia just described, excepting only the substitution of pure calcium oxide, specially prepared, for magnesium oxide.

	Weight of $NaCl$ taken.	Weight of KCl taken.	Weight of $NaCl+KCl$ found.	Corrected weight of $NaCl+KCl$ found.	Volume of amyl alcohol used: Residual. I.	II.	Total.
	grm.	grm.	grm.	grm.	cm.^{3}	cm.^{3}	cm.^{3}
(42)	0.0859	0.1126	0.2177	0.2195	20	..	100
(43)	0.1018	0.1057	0.2217	0.2235	20	..	100
(44)	0.1096	0.0962	0.2112	0.2130	20	..	100
(45)	0.0985	0.1018	0.2113	0.2130	19	..	100
(46)	0.0914	0.1104	0.1968	0.2000	20	15	100
(47)	0.0997	0.1100	0.2080	0.2089	3	7	90

	Weight of CaO taken.	Error in weight of $NaCl+KCl$ found.	Error in corrected weight of $NaCl+KCl$ found.
	grm.	grm.	grm.
(42)	0.1000	0.0192+	0.0210+
(43)	0.1000	0.0142+	0.0160+
(44)	0.1000	0.0054+	0.0072+
(45)	0.1000	0.0110+	0.0127+
(46)	0.1000	0.0050−	0.0018−
(47)	0.1000	0.0017−	0.0008−

From these results it is plain that it is a far more difficult matter to dehydrate and dissolve calcium chloride than to dehydrate and dissolve either magnesium chloride or lithium chloride. The separation of the chlorides of sodium and potassium from calcium chloride cannot be accomplished, for the quantities employed in these experiments, by a single precipitation; but the repetition of the treatment is effective. In the residues of experiments (46) and (47) calcium could not be found by the test with ammonium oxalate. In a case, therefore, in which the separation of sodium and potassium from lithium, magnesium, and calcium in one operation should be desirable, the end may probably be accomplished by means of the process here described.

Certain preliminary experiments with the nitrates of the bases under discussion indicate that these are susceptible of similar separation by the action of amyl alcohol; and the wide applicability in analytical operations of the general principle involved — the dehydrating of salts by means of amyl alcohol or other liquid of high boiling point and appropriate solvent action — can scarcely be a matter of doubt.

THE INDIRECT ESTIMATION OF CHLORINE, BROMINE, AND IODINE BY THE ELECTROLYSIS OF THEIR SILVER SALTS, WITH EXPERIMENTS ON THE CONVERTIBILITY OF THE SILVER SALTS BY THE ACTION OF ALKALINE HALOIDS.

By J. EDWARD WHITFIELD.

In the absence of trustworthy methods for the direct quantitative separation of bromine and chlorine, it is usual to employ some process for the conversion of the mixed silver salts to a common condition. Both the reduction to silver by hydrogen and the conversion of the bromide to chloride by heating in an atmosphere of chlorine are attended with loss by volatilization and mechanical transfer, and the possible inaccuracy of both the processes is such that they can scarcely be considered as available for the estimation of small amounts of either constituent in the presence of large amounts of the other.

Of all such methods the electrolytic analysis of the mixed and fused silver salts as proposed by Bolley[1] and more recently introduced and tested by Kinnicutt[2] is probably the best, though according to Finkener[3] perfect decomposition is difficult to obtain by this method and there is danger of volatilization and partial change of the silver salts in the fusion.

Kinnicutt's test analyses of the fused salts show, for silver chloride and silver bromide each by itself, errors of 0.0006 − grm. to 0.0003 + grm. on amounts varying from 0.7 grm. to 1.8 grm.; and for the mixed silver chloride and bromide errors from 0.0010 − grm. to 0.0012 + grm. with a mean of 0.0006 + grm. on weights varying from 2 grm. to 2.8 grm.

These figures represent the sum of the errors from the weighing of the fused chloride to the weighing of the deposit of silver and do not include errors made in the precipitation, filtration, transfer to the crucible, and fusion.

A method in which the decomposition of the silver salts may be effected without fusion, and which would at the same time place the errors of filtration, preparation for weighing, and subsequent electrolysis at a

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[1] Dingl., Pol. Jour., CLI, p. 46.

[2] Am. Chem. Jour., IV, p. 22.

[3] Rose-Finkener, Quant. Anal., II, p. 621.

minimum, seems to be desirable, and a promising line of investigation was suggested by Luckow's assertion[1] that from the solution of silver chloride in potassium cyanide the silver may be thrown down completely.

Luckow gives no figures, excepting a common mean of all determinations by the precipitation from the cyanide solution and the decomposition of the solid chloride on the negative pole of the battery under sulphuric acid; so that the first experiments were made to test the accuracy of the battery process under these conditions.

In experiments (1) to (5) silver chloride was the starting point. In (1) to (3) the freshly precipitated and carefully washed chloride was dried to a constant weight in a platinum dish, protected from the light, at a temperature of about 150° C., dissolved in potassium cyanide and electrolyzed after the addition of a little sodium hydrate, preliminary analyses having seemed to indicate that the presence of sodium hydrate affected the deposition favorably. In all subsequent experiments ammonia, which was found to be of equal service, was used instead of sodium hydrate.

In experiments (4) and (5) the chloride was converted, previous to electrolysis, into the bromide by solution in potassium cyanide, the addition of potassium bromide, and precipitation by sulphuric acid, as will be described later, and the precipitate redissolved in potassium cyanide, the object being to test the action of the battery upon the cyanide solution of the silver bromide.

	Ag Cl taken.	Silver found.	Silver calculated.	Error.
	grm.	grm.	grm.	grm.
(1)	0.1565	0.1177	0.1178	0.0001—
(2)	1.3004	0.9785	0.9787	0.0002—
(3)	2.2657	1.7047	1.7051	0.0004—
(4)	0.7472	0.5618	0.5624	0.0006—
(5)	0.2854	0.2133	0.2147	0.0014—

These results, as far as they go, are satisfactory. Similar tests upon the electrolysis of silver bromide and silver iodide in the cyanide solution were undertaken, but it was thought advisable to combine incidentally with the tests of the battery process an examination of the method recently proposed by Maxwell-Lyte[2] for the direct conversion of silver chloride to the bromide and thence to the iodide.

Field[3] was the first to propose a quantitative conversion of silver chloride to the bromide by digesting the former in potassium bromide, and the change of the chloride or bromide to the iodide by the action of potassium iodide upon these salts. This method has been variously criticised and finally abandoned as an inaccurate process,[4] though so

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[1] Dingl., Pol. Jour., CLXXVIII, p. 43.

[2] Chem. News, Vol. 49, p. 3.

[3] Jour. Chem. Soc., 10, p. 234.

[4] Rose-Finkener, loc. cit.

far as concerns the conversion of the chloride and bromide to the iodide Siewert[1] shows it to be exact.

Maxwell-Lyte's method of proceeding, depending upon identically the same principle which Field attempts to utilize, consists in the solution of the silver haloid salts in potassium cyanide, the addition of potassium bromide, the decomposition of the potassium cyanide by means of sulphuric acid, with the consequent precipitation and weighing of the silver bromide mixed with the iodide of the original mixture — the resolution of this precipitate in potassium cyanide, the addition of potassium iodide, the decomposition of the cyanide as before with sulphuric acid, with the formation of a precipitate, which is presumably pure silver iodide and to be weighed as such.

To convert the chloride to the bromide Maxwell-Lyte uses a weight of potassium bromide equal to the weight of the silver chloride taken, and, to change the bromide to the iodide, a weight of potassium iodide one and a quarter times as great as the original weight of the silver chloride.

In the following experiments these amounts have varied widely, but the proportion of alkaline haloid salts employed is given for each case in the tabular statement.

The starting point was generally freshly precipitated silver chloride, but in the last three cases pure silver, this being dissolved in nitric acid, precipitated with potassium bromide (two equivalents), and the precipitate dissolved in potassium cyanide, converted to the iodide in the manner described, and weighed, the object of this being to test the convertibility of silver bromide to silver iodide.

In most cases the final precipitate after weighing was electrolyzed, so as to have a more perfect control upon the results of the conversion process, and at the same time to test the battery method additionally.

The bromide and iodide of silver were precipitated hot from dilute solutions, which were cooled and allowed to stand over night to settle before filtering.

Filtrations were made by the use of the Gooch crucible with gentle pressure. The silver salts were dried directly over a low Bunsen flame at a temperature far below the melting point, and dissolved, after weighing, by introducing crucible and asbestus into a strong solution of potassium cyanide and heating, the time necessary for the solution varying from a few minutes to several hours, according to circumstances. In some cases traces of reduced silver were found with the asbestus and were recovered by treating the felt with nitric acid and washing, the filtrate and washings being added to the main solution.

The deposition of silver was made in the platinum dish of 100 cm.^{3} capacity, which held the solution, and the current found most suitable was (as Luckow originally ecommended)[2] developed by four Meidinger

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[1] Zeitschr. anal. Chem., 7, p. 469.

[2] Loc. cit.

cells of large size. With solutions of the volume named and the area of the negative electrode employed, it was found advisable not to attempt to treat more than two grammes of the silver salt.

The solution was decanted immediately on the stopping of the current, or, better, siphoned off while the battery connections were still unbroken, and washed with distilled water to prevent the solvent action of the cyanide on the deposit.

	AgCl taken.	AgBr found.	AgBr calculated.	Error.	Equivalents of K Br taken.
	grm.	grm.	grm.	grm.	
(6)	0.3260	0.4227	0.4270	0.0043 —	2
(7)	0.3093	0.4023	0.4052	0.0029 —	2
(8)	1.3801	1.8041	1.8080	0.0039 —	2
(9)	0.2091	0.2723	0.2739	0.0016 —	10
(10)	0.6846	0.8909	0.8968	0.0059 —	10
(11)	1.1625	1.5202	1.5230	0.0028 —	20
(12)	1.1734	1.5310	1.5372	0.0062 —	20
(13)	0.3501	0.4553	0.4586	0.0033 —	29
(14)	0.4178	0.5468	0.5473	0.0005 —	29

	AgCl taken.	Silver found.	Silver calculated.	Error.
	grm.	grm.	grm.	grm.
(6)	0.3260	0.2443	0.2453	0.0010 —
(7)	0.3093	......	......	......
(8)	1.3801	1.0385	1.0386	0.0001 —
(9)	0.2091	......	......	......
(10)	0.6846	0.5137	0.5152	0.0015 —
(11)	1.1625	......	......	......
(12)	1.1734	0.8829	0.8831	0.0002 —
(13)	0.3501	0.2634	0.2634	0.0000
(14)	0.4178	......	......	......

	AgCl taken.	AgI found.	AgI calculated.	Error.	Equivalents taken of K I.
	grm.	grm.	grm.	grm.	
(15)	0.6996	1.1451	1.1456	0.0005 —	2
(16)	0.7587	1.2429	1.2424	0.0005 +	2
(17)	0.6710	1.0992	1.0988	0.0004 +	10
(18)	0.2515	0.4118	0.4118	0.0000	10
(19)	0.6501	1.0646	1.0646	0.0000	10

	AgCl taken.	Silver found.	Silver calculated.	Error.
	grm.	grm.	grm.	grm.
(15)	0.6996	0.5255	0.5265	0.0010 —
(16)	0.7587	0.5691	0.5710	0.0019 —
(17)	0.6710	0.5042	0.5050	0.0008 —
(18)	0.2515	0.1892	0.1892	0.0000
(19)	0.6501	0.4892	0.4892	0.0000

	Silver taken.	AgI found.	AgI calculated.	Error.	Equivalent taken of K I.	Silver found.	Error.
	grm.	grm.	grm.	grm.			grm.
(20)	0.5418	1.1790	1.1789	0.0001 +	2	0.5417	0.0001 —
(21)	0.3750	0.8154	0.8159	0.0005 —	2	0.3746	0.0004 —
(22)	0.4078	0.8859	0.8873	0.0012 —	10	0.4077	0.0001 —

From these experiments it appears that the deposition of silver from the cyanide solution of the chloride, bromide, or iodide is exceptionally exact. The tendency of the process, however, is to yield low results, and yet, in spite of the multiplicity of operations through which the original material has been passed in the attempt to settle two questions at once, the deficiency is not very great, being 0.0005 grm. in the mean of eighteen determinations, with a maximum value of 0.0019 grm.

The conversion of silver chloride to silver bromide by the method proposed by Maxwell-Lyte, like its predecessor, is too imperfect to be worthy of trust, but the experiments indicate unmistakably that the change of silver chloride or silver bromide to silver iodide is sufficiently complete to afford the basis of a good analytical method.

The indirect estimation of chlorine and bromine, chlorine and iodine, or bromine and iodine in presence of one another may be effected satisfactorily, therefore, by precipitating both together as silver salts, filtering on asbestus, washing and drying at 150° C., weighing, dissolving the residue in potassium cyanide, and either electrolyzing the solution to determine the silver or precipitating the silver as iodide again, filtering upon asbestus, washing, drying, and weighing.

In a mixture of all three halogens the iodine is first to be separated by known methods, and the chlorine and bromine are to be indirectly estimated as described.

ON TWO NEW METEORIC IRONS AND AN IRON OF DOUBTFUL NATURE.

BY R. B. RIGGS.

THE GRAND RAPIDS METEORITE.

In the American Journal of Science (Vol. XXVIII, 3d ser., p. 297), Prof. J. R. Eastman called attention to an iron of probably meteoric origin, found near Grand Rapids, in Walker Township, Kent County, Michigan.

At the time a rough analysis was made on scanty material, identifying it as a true meteoric iron. Since then the iron has come into the keeping of the National Museum and a more careful analysis has been made, with the following results:

	Per cent.
Fe	88.71
Ni	10.69
Cu	.07
Mg	.02
P	.26
S	.03
C (combined)	.06
Graphite	.07
	99.91

The meteorite weighed originally about 52 kilograms. It is a compact mass of great apparent homogeneity, possessing a specific gravity of 7.87. One of the sections disclosed, however, a small nodule about one centimeter in diameter. This not being available for analysis, its composition remains undetermined.

Etched with nitric acid, the iron gives Widmanstättian figures very like those of the Robertson County meteorite, though of a finer character. No fracture lines were observed.

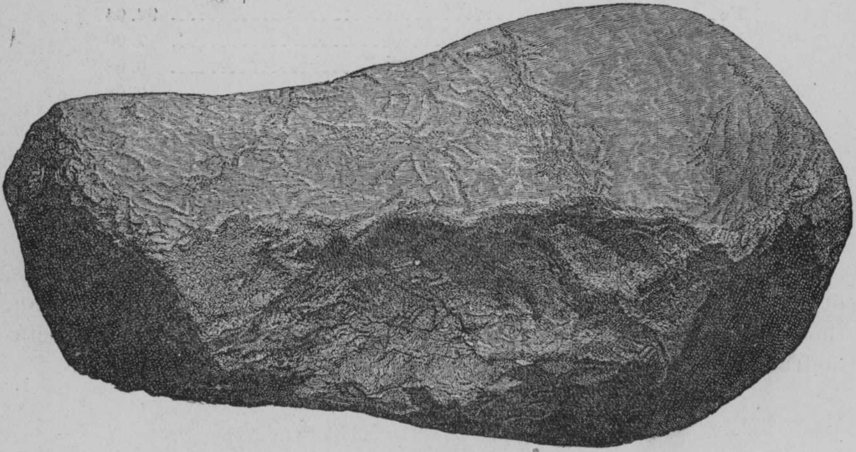

FIG. 4. Grand Rapids meteorite.

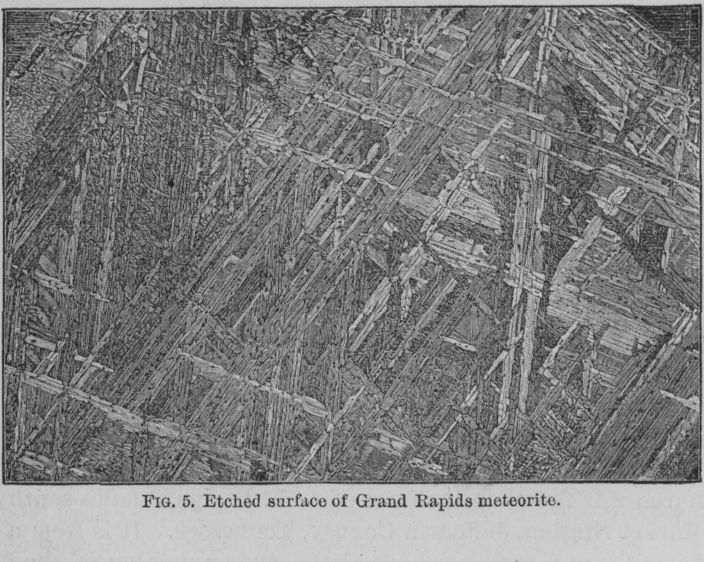

FIG. 5. Etched surface of Grand Rapids meteorite.

THE ABERT IRON.

This meteorite was found unlabeled in a collection of minerals made by the late Col. J. J. Abert, and was presented to the National Museum by his son, Mr. J. T. Abert. The iron, evidently not a fragment, weighed originally 456 grammes, and had a specific gravity of 7.89. A cross section measured 50 by 37 millimeters.

An analysis gave it the following composition:

	Per cent.
Fe	92.04
Ni	7.00
Co	0.68
P	0.08
S	0.01
C (combined)	0.02
Graphite	0.03
	99.86

Nitric acid brought out very characteristic Widmanstättian figures, of the same octahedral marking with, though somewhat coarser than, those of the Grand Rapids meteorite. The fracture is distinctly octahedral.

FIG. 6. Etched surface of Abert meteorite (actual size of section).

AN IRON OF DOUBTFUL NATURE.

This iron was found on the farm of A. L. Hodge, 3 miles southwest of New Market Station, Jefferson County, Tennessee. It is from a region full of small iron furnaces, whence have come a number of the pseudometeorites, among others the Hominy Creek, Rutherfordton, and Campbell County irons. Special inquiries were therefore made by Prof. Ira Sayles, who obtained the specimen, regarding the presence of furnaces in the vicinity. So far as could be learned, that locality was free from them. Full of cavities, the iron is characterized by great hardness, defying the use of saws. With a specific gravity of 7.61, it weighed 640 grammes. Fragments, however, had evidently been broken off from it.

The following are the results of an analysis:

	Per cent.
Fe	88.27
Ni	0.76
Co	0.19
Cu	0.03
As	Trace
Mn	6.73
Mg	0.14
P	1.80
Si	0.15
C (combined)	1.46
Graphite	0.86
	100.39

Treated with nitric acid, the polished surface developed quite fine markings not unlike Widmanstättian figures.

Its high percentage in manganese is possibly an objection (not by any means all sufficient) to ascribing to it a meteoric origin. The presence of manganese, and in considerable quantities, is not so uncommon as many think. The Claiborne and Bitburg meteorites, both of unquestioned origin, contain respectively 3.24 per cent. and 4 per cent. Furthermore, while the presence of nickel and cobalt proves nothing, so large an amount of phosphorus is not common in a furnace product.

THE EFFECT OF SUDDEN COOLING EXHIBITED BY GLASS AND BY STEEL, CONSIDERED BOTH PHYSICALLY AND CHEMICALLY.[1]

By C. Barus and V. Strouhal.

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§ I. THE STRAIN IMPARTED BY SUDDEN COOLING, AND ITS RELATIONS TO TEMPERATURE.

INTRODUCTION.

In Bulletin 35 we communicated a series of results on the structure of steel of a given kind, tempered hard. They showed, in general, that from the circumference to the axis of a quenched, non-filable, steel cylinder hardness continually diminishes; that the first filable strata are encountered at a distance of about 1^{cm} below the surface. Moreover, as hardness decreases, the density of the elementary conaxial cylindrical shells increases, and in proportion as the layers become more and more nearly or easily filable the density is found to approach the density of soft steel. From an examination of rods of different diameters (2^{cm} to 3^{cm}) it appears, steel of a given kind presupposed, that the hardness at a point is essentially dependent on the distance of the point below the surface. The rate at which sudden cooling takes place must be similarly conditioned. Hence it is permissible to associate the one phenomenon with the other and to state that the hardness in a given point below the surface is dependent on the rate at which cooling there takes place. This point of view is suggestive; structure investigations may be made to furnish us the best means we know for the comparison of hardness and rate of cooling.

The results cited apparently make sad havoc with physical theories of temper. They seem indeed to be fatally at variance with the usually accepted views, viz: that in hard tempered steel an abnormally dense shell is arched around an abnormally rare core, the two states of strain mutually conditioning each other. The data may even be looked upon as furnishing evidence sufficient to prove the total absence of strain. It is the object of the present section to investigate in what measure this evidence is critically sufficient; if it be insufficient, to state the nature and relations of the strain effect of quenching somewhat more clearly than we were able to do in our earlier work.

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[1] Our earlier work on the iron carburets will be found in Bulletins Nos. 14, 27, and 35.

In our little book on the iron carburets[1] we endeavored to contrast the respective merits of chemical and physical theories of temper, using for this purpose all the data known to us, as well as special results of our own. The deduction seemed warranted that hardness and strain are distinct and separate properties of a tempered iron carburet;[2] that they need not necessarily coexist. Leaving therefore hardness pure to be explained chemically, we inferred that the category of electrical and magnetic phenomena exhibited by steel on passing from hard to soft are mainly referable to changes in the character and intensity of the strain which the tempered rod carries. We accepted the theory of a dense shell and a rare core as being the most satisfactory and elegant conception of the strain in question, with the proviso[3] that "it must be regarded as a mere *diagram* of the essential features of the vastly more complicated structure of the glass-hard rod." These conditions premised, we finally interpreted all variation of strain produced by annealing as the combined effect of changes of the viscosity of steel due to temperature and of interference of thermal expansion with the said strain.

The experimental question which we are endeavoring to elucidate may therefore be succinctly put as follows:

(1) With what degree of sensitiveness do the variations of the density of the rod, as a whole, indicate the corresponding variations of strain?

(2) Is it possible successively to remove layer after layer of a rod without materially changing the character and intensity of the strain which the rod is supposed to carry?

(3) In how far does the actual structure of tempered steel differ from the diagrammatic distribution of density above assumed?

(4) Does the process of sudden cooling impart strain alike in kind[4] but differing enormously in degree to all substances?

In our paper on structure we had the second and third of these points principally in mind. We were unable to obtain direct and decisive evidence of the occurence of shrinkage during the removal of shells from a hard steel rod. But since the structure of steel differs so largely with the kind of steel operated upon, we do not regard our experiments as made in sufficient number to be conclusive. An examination of the density of the elementary shells shows that the character of the density at any point regarded as a function of the distance of a point below the surface is harmonic.[5] To investigate this relation it is unfortunately necessary to make the measurements for thin ($\frac{1}{2}^{mm}$) shells. Hence the

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[1] Bull. U. S. Geol. Surv., No. 14, p. 76, 1885.

[2] Id., pp. 103, 197

[3] Bull. U. S. Geol. Surv., No. 14, pp. 95–98

[4] We do not necessarily refer to mere volume expansion here. See Wrightson, Jour. Iron and Steel Inst., II, p. 418, 1879.

[5] Bull. No. 35, U. S. Geol. Surv., p. 32, 1886.

mean amplitude of vibration and the limits of the unavoidable errors of observation are of the same order. To discriminate between the periodic effect of temper, which may show regular or irregular periodicity, and the apparently periodic distribution of mere errors of observation is difficult and requires very nice and careful observation. In Bulletin 35 we attempt to arrive at this discrimination by making minute comparisons of the structures of rods of the same kind of steel and of the same or of different diameters. This procedure is excessively laborious; it calls for a detailed construction of the relation of the density and the position of the points along any given radius of the rod and subsequent examination of the properties which the divers diagrams have in common. We have gathered many data, but the work is as yet incomplete, and the reader desiring further information will have to be referred to Bulletin 35, where the whole subject is discussed. Experiment on the fourth of the above topics we have now in progress and shall publish later. This narrows the purposes of this paper to the consideration of the first and most important of the above points, viz: In what degree the density of a hard steel rod at different points, even when measured with all attainable accuracy, is sufficiently sensitive to represent the character, relations, and intensity of the temper strain.

DENSITY AND RESISTANCE (STRAIN) OF TEMPERED STEEL.

Experimental results.—The discussion may be appropriately commenced by an examination of the variation of density of steel successively annealed from hard to soft. Our experiments on this subject, made in some number, are detailed in Bulletin No. 27, U. S. Geological Survey, and from this we select a digest of data sufficient for the construction of the following graphic comparison, a comparison which did not fall properly within the scope of the inquiry in Bulletin No. 27, and hence was there omitted. It is necessary to reiterate that the dimensions of the steel rods used were as follows:

TABLE I.

No.	I.	II.	55 to 60 61 to 63	0.	36 to 36.
Average length of pieces (cm)	5. 3	10. 1	2. 5	2. 5	2. 5
Number of pieces (cm)	1	1	21	18	72
Diameter (cm)	1. 9	0. 58	0. 13	0. 23	0. 08

It was our constant endeavor to so anneal as to exclude all errors due to superficial oxidation and carburation. Whether this was accomplished remains to be seen. In Fig. 7 the temperature at which the rod was annealed is given as abscissa, the corresponding density as ordinate.

The commercial density for the respective cases is indicated by an attached *c*.

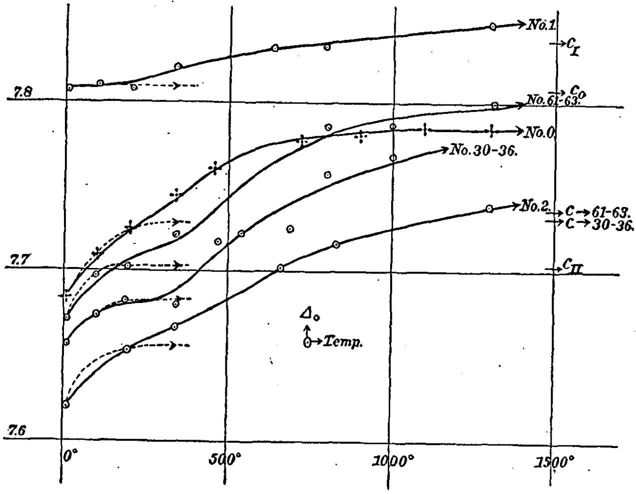

FIG. 7. Diagram showing variation of the density of steel, with temperature of annealing.

Discussion.—We advert in passing to the fact that, whereas density increases continually on passing from hard to soft, resistance passes through a pronounced minimum.

Whether we regard Δ_0 as a function of resistance or of the temperature t° at which the rod was annealed, the relations investigated lead to an important inference with an immediate bearing on our present purposes. It appears plainly that *the annealing of a rod successively from extreme hard to extreme soft does not exhibit the characteristics of a single and homogeneous phenomenon.* This annealing presents two distinct and independent phases, which merge into each other when t° corresponds to incipient redness. The graphic representation of Δ_0 varying with t° shows this transition with singular clearness. Between $t^\circ = 200$ and $t^\circ = 500$ all the loci pass through two consecutive circumflexures in such a way as to change the general and pretty uniform contours of concavity downwards into convexity downwards for the interval in question. The division of the complete phenomenon into two parts being thus suggested, we find on further inspection that the variations of the electrical constants of temper subside almost completely within the first of these parts (annealing between 0° and 350°); whereas in the second part (annealing between 350° and 1,000°) they become crowded and complex. It follows plausibly and at once that during the first of the phases under consideration we encounter the subsidence of a mechanical strain. This inference gains much in weight when we find that this strain vanishes, in the way peculiar to phenomena of viscosity, at a slowly decreasing rate, through infinite time.[1] In the sec-

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[1] In other words, the temper strain vanishes just like the simple "drawn" strains imparted by the wire plate while the wires carrying them are each exposed to the prolonged action of temperature.—Bull. No. 14, U. S. Geol. Surv., p. 93.

ond phase, mechanical and chemical occurrences are superimposed and the above results do not enable us to disentangle them.

The final important deduction from the data is this, that during the first phase, in which the larger values of resistance are from two to three times the smaller values, the variation of density is slight. In the second phase we encounter large variations of density associated with small variations of resistance.

These curious relations characterize the phenomenon as a whole. We shall interpret them partially at least below.

DENSITY AND STRAINS IN TEMPERED GLASS.

Experimental results.—This result substantiates the evidence in favor of the existence of strain in hard steel adduced in our earlier papers.[1] Beyond this it shows almost conclusively that the density effect of the annealing of hard steel is out of all proportion and symmetry with the strain effect and the corresponding electrical effect. We were desirous, therefore, of studying the temper strain in substances other than steel and free from carbon. Long ago glass had suggested itself to us for this purpose.[2] We communicate in the following Table II the density effect produced by successive annealing of ordinary Prince Rupert drops. Twelve of these were in hand. Three were broken to test the strain, the remainder examined. All the drops contained included bubbles, one or more, often 0.2^{cm} to 0.3^{cm} in diameter and distributed irregularly. Usually a few large bubbles predominated. The drops moreover showed a purple coloration, which disappeared after annealing at incipient redness.[3] To anneal the drops at different temperatures we inclosed them in a test tube, cushioned upon and surrounded by carded asbestus. The end of the tube was submerged sufficiently to cover the Prince Rupert drops in boiling camphor, mercury, sulphur, &c., as given in the table. To anneal at red heat, the drops were suspended in little baskets of platinum foil, in the center of large thick clay crucibles, and then heated to the desired temperature in an assay furnace. Under all circumstances but one care was taken, to cool the drops slowly. Table II contains under "temper" the temperature and time of annealing, not including the time of cooling, however. The column m gives the weight of each drop in grammes. Variations of m are due to accidental breakage of the frail stems of the drops. Where no such breakage occurs m is constant. Δ_t is the density of the drops at t°; Δ_0, finally, is the density of the drops at 0° C., under the conditions given. Each Δ_0 is the mean of two independent determinations and is correct to within one or two units of the third place.

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[1] Bull. No. 14, U. S. Geol. Surv., pp. 88–103.

[2] Wied. Ann., VII, p. 406, 1879.

[3] The color of the drops is amethystine. Mr. R. B. Riggs, of the U. S. Geological Survey, kindly analyzed the glass and found manganese.

TABLE II.—*Temper, weight, and density of quenched glass (Prince Rupert drops) successively annealed.*

No.	Temper.	m	t	Δ_t	Mean Δ_0	Remarks.
			°			
1	Quenched	1.3500	17.9	2.4336	2.4345	Bubbles; color.
		1.3501	17.0	2.4333	....	
	Annealed, 360°, 30^m (mercury)	1.3500	15.6	2.4388	2.4401	Do.
		1.3500	15.8	2.4394	....	
	Annealed, 600°, 10^m	1.3497	14.8	2.4894	2.4901	Bubbles and color vanish. Slow cooling; form of drop not changed.
		1.3496	15.3	2.4890	....	
	Annealed, red heat	1.3470	18.0	2.4901	2.4910	Slow cooling.
		1.3470	18.0	2.4896	....	
	Annealed, red heat	1.3311	18.4	2.4872	2.4883	Cooled in air.
	Annealed, red heat	1.3312	18.2	2.4904	2.4915	Cooled slowly.
2	Quenched	1.3200	17.5	2.4354	2.4364	Bubbles; color.
		1.3201	16.8	2.4354	....	
	Annealed, 360°, 30^m (mercury)	1.3201	15.7	2.4392	2.4408	Do.
		1.3200	15.8	2.4404	....	
	Annealed, 600°, 10^m	1.3191	15.1	2.4898	2.4903	Bubbles and color vanish; slow cooling; form of drop not changed.
		1.3190	15.5	2.4891	....	
	Annealed, red heat	1.3172	18.5	2.4901	2.4912	Slow cooling.
3	Quenched	1.4590	15.9	2.4364	2.4374	Bubbles; color.
		1.4590	16.0	2.4364	....	
	Annealed, 200°, 15^m (paraffine)	1.4591	15.9	2.4354	2.4364	Do.
	Annealed, 360°, 30^m	1.4590	16.5	2.4403	2.4411	Do.
		1.4590	16.9	2.4399	....	
4	Quenched	1.3305	16.0	2.4345	2.4356	Bubbles; color.
		1.3304	16.0	2.4348	....	
	Annealed, 200°, 15^m	1.3305	16.3	2.4341	2.4351	Do.
	Annealed, 360°, 30^m	1.3292	16.7	2.4369	2.4383	Do.
		1.3292	17.0	2.4378	....	
5	Quenched	1.3009	16.8	2.4333	2.4349	Do.
		1.3010	16.8	2.4344	....	
	Annealed, 200°, 1^h 30^m (camphor)	1.3009	15.9	2.4349	2.4359	Do.
	Annealed, 360°, 1^h (mercury)	1.3010	16.5	2.4390	2.4402	Do.
		1.3010	16.8	2.4394	....	
	Annealed, 450°, 30^m (sulphur)	1.3012	17.3	2.4441	2.4446	Do.
		1.3012	17.4	2.4431	....	
	Annealed, 550°, 10^m	1.2983	16.2	2.4521	2.4531	Color vanishes; slow cooling.
	Annealed, red heat	1.2982	17.5	2.4906	2.4914	Bubbles vanish; form of drop partially changed.
		1.2983	17.8	2.4900	....	
6	Quenched	1.4409	16.8	2.4312	2.4323	Bubbles; color.
		1.4408	16.9	2.4315	....	
	Annealed, 200°, 1^h 30^m (camphor)	1.4409	16.0	2.4323	2.4333	Do.
	Annealed, 360°, 1^h (mercury)	1.4409	16.7	2.4370	2.4382	Do.
		1.4409	16.9	2.4374	....	
	Annealed, 450°, 30^m (sulphur)	1.4412	17.1	2.4410	2.4422	Do.
		1.4412	17.4	2.4414	....	
	Annealed, 550°, 10^m	1.4410	16.4	2.4524	2.4534	Color vanishes; slow cooling.
	Annealed, red heat	1.4408	17.7	2.4878	2.4893	Bubbles gone; form of drop partially changed; slow cooling.
		1.4407	17.9	2.4885	....	
7	Quenched	1.4795	16.2	2.4385	2.4395	Bubbles; color.
		1.4795	17.6	2.4385	....	
8	Quenched	1.0024	16.3	2.4389	2.4395	Do.
		1.0026	17.6	2.4381	....	

TABLE II.—*Temper, weight, and density of quenched glass, &c.*—Continued.

No.	Temper.	m	t °	Δ_t	Mean Δ_0	Remarks.
	Annealed, 360°, 30^m (mercury)	1.0025	17.4	2.4434	2.4444	Bubbles; color.
		1.0025	17.5	2.4434	....	
	Annealed, 360°, 3^h (mercury)	1.0023	16.8	2.4474	2.4482	Do.
		1.0023	17.3	2.4471	....	
	Annealed, 450°, 1^h (sulphur)	1.0023	18.2	2.4515	2.4526	Do.
		1.0023	16.2	2.4515	....	
	Annealed, 450°, 4^h (sulphur)	1.0023	16.5	2.4579	2.4586	Do.
		1.0023	16.8	2.4574	....	
	Annealed, red heat	0.9982	18.5	2.4890	2.4901	Bubbles and color gone; form partially changed; slow cooling.
9	Quenched	1.2758	17.0	2.4363	2.4365	Bubbles; color.
		1.2760	17.6	2.4346	....	
	Annealed, 360°, 30^m (mercury)	1.2746	17.4	2.4410	2.4423	Do.
		1.2744	17.5	2.4416	....	
	Annealed, 360°, 3^h	1.2745	17.0	2.4425	2.4436	Do.
		1.2745	17.4	2.4427	....	
	Annealed, 450°, 1^h	1.2745	18.2	2.4461	2.4472	Do.
		1.2745	18.3	2.4461	....	
	Annealed, 450°, 4^h	1.2727	16.7	2.4499	2.4510	Do.
		1.2727	16.8	2.4501	....	
	Annealed, red heat	1.1592	18.4	2.4918	2.4929	Bubbles and color gone; slow cooling; form of drop partially changed.

Table III, following, is constructed to facilitate a comparison of the important data. The second and third columns contain the densities of the extreme states of temper, the original quenched, "hard," and the final "soft," or thoroughly annealed state. The remaining columns contain the increments of density due to quenching, relative to the density of the soft state, the relative increments, in other words, which are retained at the divers temperatures given.

TABLE III.—*Summary showing density of Prince Rupert drops, quenched and annealed.*

No.	"Hard." Δ_0.	"Soft." Δ_0.	Density increment relative to "soft," when annealed at—						
			20°.	200°.	360°.	450°.	(550°.)	(650°.)	Red heat.
1	2.4345	2.4915	−0.0229	....	−0.0207	....	....	−0.0006	−0.0002
2	2.4364	2.4912	−0.0222	....	−0.0202	....	....	−0.0004	−0.0000
3	2.4374	....	−0.0216	−0.0220	−0.0201	....	....	....	....
4	2.4356	....	−0.0223	−0.0225	−0.0212	....	....	....	....
5	2.4349	2.4914	−0.0227	−0.0223	−0.0206	−0.0188	−0.0154	....	−0.0001
6	2.4323	2.4893	−0.0229	−0.0225	−0.0205	−0.0189	−0.0144	....	+0.0007
7	2.4395	....	−0.0207	....	....	....	....	....	....
8	2.4395	2.4901	−0.0203	......	−0.0184	−0.0150	....	....	+0.0004
					−0.0168	−0.0127	....	....	....
9	2.4365	2.4929	−0.0227	......	−0.0203	−0.0184	....	....	−0.0007
					−0.0198	−0.0168	....	....	....

Discussion.—The salient features of these data are obvious from an inspection of Table III. The density effect of quenching is decidedly *negative*, the increase of specific volume is exceptionally large. Moreover, the nine[1] Prince Rupert drops examined exhibit nearly the same initial density and nearly the same final density. The approximate equality of the values Δ_0 for the soft state is easily explained. It indicates that in proportion as we bring the strain to vanish we reach the normal density of the glass. It is not so easy to account for the observation that the density of the Prince Rupert drops shows almost the same degree of equality in the hard (quenched) state. Indeed, if we take the fact into consideration that the drops invariably contain *bubbles* distributed irregularly, and without apparent relation as regards size and number, the difficulties of explanation are increased. In other words, it is an exceedingly striking and important result that the volume increase due to quenching is quite as much the same for all drops as is at all possible for the case of so complicated an operation. We are thus led to this inference: Inasmuch as bubbles are present in like total volume in each of the drops, their presence cannot be a circumstance of mere accident; they must be regarded as a normal effect, or, better, a necessary result of the operation of quenching applied to glass; they must in some very intimate way be connected with the strain which the glass globules have experienced in virtue of sudden cooling.

Retaining this very reasonable surmise in mind, we proceed to a more minute inspection of the effect of annealing the hard Prince Rupert drops. We obtain results very similar to those investigated above for steel. The density effect of annealing is decidedly positive, and is greater as temperature and time of exposure are increased. Again, we readily divide the physical effect of annealing into two parts or phases. The first of these corresponds to the annealing temperatures 0° to 500°, the other to higher temperatures. The range of temperatures corresponding to the first phase is therefore larger for glass than for steel; and if we compare Tables I and II it appears obviously that for like density effects the annealing temperatures must be chosen higher in the former case (glass) than in the latter. But the change of density encountered in both instances is small; and yet, in spite of the small density effect during the inferior stage of annealing, by far the greater intensity of strain vanishes. The drops after annealing at 200° are still explosive; if they be broken after having been annealed in boiling sulphur at 450° they are found to have lost all traces of the explosive properties which the originally quenched drops possessed. Professor O. N. Rood[2] informed us that the polarization figures could be quite wiped out by annealing such ordinary glass as exhibited them only as far as the temperature of melting zinc. We infer that at the end of the first

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[1] Further (incidental) examples are given in the next section, p. 115.

[2] Results obtained by Professor Rood during his experiments with high vacua.

phase of annealing we have in hand a hollow glass globule practically free from strain.

During the second phase of the annealing phenomenon (500° to 1000°), we observe a very pronounced change of the density of the Prince Rupert drops, corresponding to the above result for steel. But the explanation is here readily at hand; at incipient redness the inclosed bubbles *disappear* or are reduced to mere specks. The large increment of density in question is therefore nothing more than an expression for the collapse of the viscous hollow globule in virtue of atmospheric pressure. This important observation enables us to interpret all the phenomena of annealing satisfactorily. It must therefore be carefully examined.

We shall endeavor to prove that the bubbles are vacua, that they are not accidental inclusions of gas or aqueous vapor. The temperature from which glass is quenched is certainly less than 1500°. The temperature at which glass is sufficiently viscous to yield easily to atmospheric pressure is certainly greater than 500°. Suppose now that the changes of volume of the bubble were the result of thermal expansion of an included gas. Let v_{1500} and v_{500} be the volumes of the gaseous inclusion at 1500° and 500°, respectively, under normal pressure. Let v_h and v_s be the volumes of the gas bubble for the quenched (hard) and annealed (soft) states. Then we deduce, a fortiori,

$$\frac{v_h}{v_s} < \frac{v_{1500}}{v_{500}} = 2.3 \tag{1}$$

With this as a point of departure the following little digest of mean results, Table IV, has been prepared. Here m is the mean mass of all the drops examined; Δ_h, Δ_s, V_h, V_s, their mean density and total volume for the hard and the soft states, respectively; v is the mean volume; r the equivalent mean radius of the bubbles. In the second horizontal row V_h has been diminished one-half per cent., to refer all volumes to the beginning and end of the second phase of annealing.

TABLE IV.—*Mean volume relations of the Prince Rupert drops and of the hypothetical gas bubble.*

V_h	V_s	v at—		r at—		
		1500°.	500°.	1500°.	500°.	
cc.	*cc.*	*cc.*	*cc.*	*c.*	*c.*	
0.5454	0.5334	0.0120	0.0052	0.142	0.107	$\frac{v_h}{v_s}<2.3$
0.5427	0.5334	0.0093	0.0041	0.130	0.099	$\frac{r_h}{r_s}<1.3$

Mean $m = 1.3288$ g

"Hard:" Mean $\Delta_h = 2.4363 \pm 0.0008$

"Soft:" Mean $\Delta_s = 2.4911 \pm 0.0016$

Inasmuch as the values v_{500} and r_{500} are inferior limits, it is clear that, if the bubbles were gas or vapor, they would be of the same order of visibility before and after annealing. In other words, if the bubbles were gas, casual inspection would not detect a difference of their size in the "hard" (quenched) and in the "soft" drops. In the experiments, however, the bubbles all but vanish. Hence they cannot be gas.

To obtain additional assurance on this point we ground flat faces on the annealed drops Nos. 1, 5, and 8, and then measured the size of the inclusions. We found these values:

No. 1: $v_s = 0.000037^{cc}$.
No. 5: $v_s = 0.000062^{cc}$.
No. 8: $v_s = 0.000040^{cc}$.
Mean: $v_s = 0.000046^{cc}$.

From actual measurement therefore we find

$$\frac{v_h}{v_s} > 100 \qquad (2)$$

a result wholly incompatible with $\frac{v_h}{v^s} < 2.4$, as derived above (Table IV). It follows conclusively that the bubbles are not accidental gas inclusions and that only an insignificant part of the variations of volume produced by quenching can be referred to thermal expansion of gas.

If the gas were aqueous vapor and if dissociation were complete, then the upper limit of (1) would have to be increased in the ratio of 3:2. This does not remove the discrepancy between (1) and (2). Moreover, since dissociation of water is only incipient at 1500°, and is not even complete at the temperature of melting platinum, the volume variation of the bubbles cannot be due to the presence of water in the bubbles.

If, on the other hand, we endeavor to explain the bubbles as vacuities[1] left by the contracting glass, we arrive at accordant and reasonable results. Let t be the temperature to which the homogenous glass drop must be heated in order that the observed mean volume of the soft state may be equal to the observed mean volume of the hard state. Then, since volume increases at an accelerated rate with temperature,

$$t < \frac{1}{3\alpha} \frac{\Delta_0 - \Delta_t}{\Delta_t} \qquad (3)$$

where α is the ordinary coefficient of linear expansion of glass. By inserting the values of Table III into (3) we derive

$$t < 900^\circ.$$

In other words, the quenched globule has retained the volume which the hot glass possessed at a temperature certainly smaller than 900°. This result taken together with the other is conclusive (see p. 112).

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[1] Very analogous to Torricellian vacua.

The general result of our investigation on the process of sudden cooling, therefore, points out the fundamental importance of a rigid shell. As the material (glass or steel) cools, contraction as a whole takes place not centripetally but centrifugally, i. e., not towards the center of the figure, but away from it. So long as the interior remains liquid or viscous, the result is simple separation, commencing at points where minute air bubbles may pre-exist,[1] rather than at points of the continuity of glass. The final result is a vacuum bubble such as we have observed. In proportion as the interior becomes rigid the temper strain appears. Should the glass hold gases in solution, they would tend to escape into the vacua in question. There is probably another reason why in most instances the bubbles cannot be brought completely to vanish. Annealing reverses the whole phenomenon. The small changes of density observed in the first phase may be easily accounted for: it is probable that during these stages of annealing the rearrangement of molecules and disappearance of strain are accompanied by expansion inward toward the vacua. Hence the incommensurately small variation of mean density which accompanies the great optical effects (glass) and the great electrical effects (steel).[2] During the second stage of annealing, again, the density effect is incommensurately large; for glass it is the expression of a mere collapse, due to the atmospheric pressure. At all events the density effect (error) due to bubbles quite swallows up the density effect due to strain. Hence to represent the true relation of density and resistance or of density and annealing temperature in case of steel, it may be necessary to lower the part of the curves corresponding to the second phase of annealing by amounts equivalent to the bubble or fissure discrepancy, or else for like reasons to raise the parts of the curves corresponding to the first phase. If this be done, the circumflexures become less pronounced or disappear, and the points for the commercial soft state are more easily referred to the curves to which they belong. If, therefore, allowance be made for the distortion due to internal sensible pores, the relations become more uniform.

It is interesting to observe that glass retains the volume expansion corresponding to a temperature somewhat below 900°, whereas steel retains the volume expansion of a temperature below 400°. Similarly, the strain in steel is very perceptibly affected by annealing temperatures as low as 50°, whereas for glass the perceptible annealing effects are only incipient even at 200°. The amount of strain retained is, cæteris paribus, not merely a function of the viscosity of the material subjected to

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[1] Prince Rupert drop No. 1, heated intensely in a blast lamp and cooled in air, shows a decrement of density. This is due to the rapid cooling; for when this drop is heated and cooled in the crucible, density is again incremented. The experiment shows the tendency of glass to retain strains. During the heating to 1000° no expansion of the very small bubbles was observable.

[2] The electrical and optical criteria may be considered equally sensitive.

quenching; it must depend also on the heat conductivity of this substance. For instance, if like figures of glass and of steel be quenched alike, then at the same time and depth the thermal gradient would be much steeper in the case of glass than in the case of steel. Hence, cæteris paribus, during quenching a rigid shell is possible in the case of glass for higher temperatures of the core than in the case of steel. The sudden contraction of the shell (pressure) has a marked effect on the melting point or degree of fluidity of the core. But it is best to waive this observation here, for the want of data to interpret it.

We have finally to consider the bearing of the results of this paper on the structure of steel. The detailed similarity observed in the annealing of glass and of steel suggests the inference that the interior of hard steel may be sensibly fissured. Under all circumstances the diagrammatic structure of dense shell and rare core would be inaccurate to the extent in which these fissures are irregularly distributed. Hence the difficulty of developing the true character of the dependence of the density (δ) at any point upon the distance of this point below the surface. We are able to account in part for the quasi-harmonic relations obtained both by Dr. Fromme[1] and by ourselves.[2] While the consecutive shells are being removed by solution, periodic fluctuation of δ must result whenever fissures are invaded. If, furthermore, we take into consideration that the density effect of even great intensities of temper strain is small, it appears that the true nature of the strained structure of tempered steel may be beyond the discernment of the density method of investigation altogether. The *gross* variation of density along the radius is a carburation phenomenon.

POLARISCOPIC OBSERVATIONS.

In this place we desire to substantiate the earlier inferences of this section and to give sharper expression to them. We therefore repeat Professor Rood's experiments on the polariscopic effect of continuous annealing of cooled glass at low temperatures. Our object is merely to detect variations in the polarization figure produced by annealing or, later in our work, by the removal of superficial shells. Hence it is sufficient to examine the drops in a given fixed position between polarizing plates.[3] Disturbances due to diffuse refraction are satisfactorily eliminable by submerging the Prince Rupert drop in glycerine, the refractive power of which is nearly that of the glass. The demarkation is then distinct and the colors clear, so that the figures can easily be drawn. The necessity of grinding special faces or plates is thus fortunately obviated, for in case of the quenched drop such operations are not feasible.

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[1] Wied. Ann., VIII, p. 356, 1879.

[2] Bull. No. 35, U. S. Geol., Surv. p. 36.

[3] We are indebted to Professor Hitchcock for the use of a simple but efficient reflecting polariscope, formerly the property of Professor Joseph Henry.

In the case of simple annealing, variations of the polarization figure are due to a diminution of what we may loosely call the birefractive power of the Prince Rupert drop. In the case of removal of shells, as described in the next section, variations of figure result from diminution of thickness, possibly associated with diminution of birefractive power. The solution of the drop in hydrofluoric acid does not materially interfere with its transparency. The optic observations may therefore be continued indefinitely.

Our polariscopic experiments were made with the Prince Rupert drops Nos. 1, 2, 4, 6, and Nos. 3, 5, 7, 8, 9. The first four of these were simply annealed, the remainder[1] examined after consecutive removals of shells. It is expedient to describe only the experiments with annealed drops in this section. These experiments are so striking and so easily repeated, on the one hand, and so difficult to reproduce accurately in a drawing, on the other, that the following very careful free hand sketches of the main features of the figures are here inserted, principally for purposes of record. The cuts represent Prince Rupert drops Nos. 1, 2, 4, and 6 in fixed position between nicols.

On annealing as far as $T = 200°$, variations of figure are not certainly perceptible. After very long annealing at this temperature (200°) a faint influence appears, but is restricted to changes of color. It is particularly to be observed that the position and contours of the original polarization figure show a very obvious relation to the position of the included bubbles (black spots in the figure). This was the invariable result for all the Prince Rupert drops examined. It is in accord with our inference of "centrifugal" contraction,[2] discussed above. At 200°, therefore, change of strain in glass is incipient. The Prince Rupert drop, if broken, is still explosive, though perceptibly less so than the original drop.

After one hour of annealing in boiling mercury (360°) the changes of the polarization figure are obvious. The whole appearance is more diffuse, the colors bolder and broader, and the demarkation less distinct and delicate. These striking observations can only partially be reproduced in a figure. We have encountered very marked diminution of birefractive power. After seven hours of annealing in boiling mercury the evidences of diminished birefractive power have visibly increased. The figures as a whole are simpler, the coloration more gross.

Finally, after annealing in boiling sulphur (450°), the polarization figure has wholly vanished; we have in hand a hollow glass globule, free from æolotropic strain. We show on page 121 that the substance of the Prince Rupert drop is under a strain of dilatation. It is necessary to bear in mind that the isotropic part of this strain is not demonstrable by optic means. The drop annealed at 450°, however, has wholly lost its explosive character.

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[1] § II, p. 116.

[2] § I, p. 108.

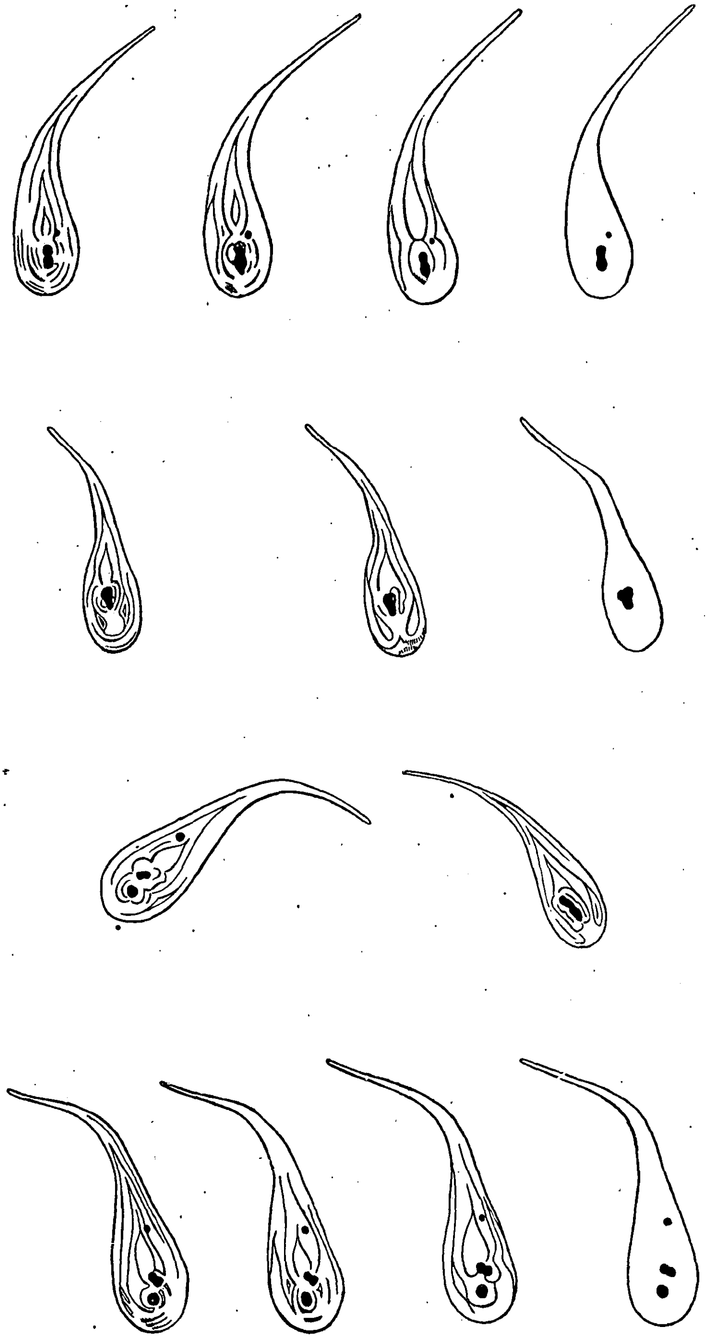

FIG. 8. Polarization figures of Prince Rupert drops.

Here we encounter the first important analogy between the optical behavior of quenched glass and the electrical behavior of quenched steel. We shall show that this parallelism extends even into details. Change of strain in glass is incipient at 200°, in steel at 50°. Change of æolotropic strain in glass is complete at a temperature certainly greater than 350° and less than 450°. The corresponding superior limit for steel cannot be so well defined. In both cases the essential dependence of the result to be reached on the temperature and the time of annealing (asymptotic relations) is the marked feature of the pheuomenon.

§ II. THE STRAIN IMPARTED BY SUDDEN COOLING, AND ITS STRUCTURAL RELATIONS.

In the last section we compared the strains experienced by glass and by steel on sudden cooling by aid of the density variations observed on annealing the bodies carrying strain *as a whole*. Our purpose in this section is to investigate the density relations of consecutive similar shells of the Prince Rupert drop and the optical character of the successive cores. Availing ourselves of all the evidence adduced in our investigation at its present stage, we endeavor again to show that the optical effect of the temper strain in glass may be regarded as the precise analogon of the electrical effect of the temper strain in steel.

CERTAIN GENERAL PROPERTIES OF THE PRINCE RUPERT DROP.

It is well known that mere breakage of the tail of a Prince Rupert drop is sufficient to shatter it; the splinters fly apart with explosive violence. It is not so well known that the same drop may be dissolved in hydrofluoric acid to a mere spicule without exploding.[1] This peculiar behavior calls to mind certain properties of nitroglycerine, inasmuch as this substance may be burned off quietly in a wick but explodes on percussion. It is in keeping, moreover, with Dr. F. A. Gooch's ingenious suggestion that in the quenched globule we may possibly encounter a polymerization of the molecular structure of the annealed globule. But the fact that the strain is of an ordinary mechanical kind is proved by the observations of Table V, in which the behavior of Prince Rupert drops from which different thicknesses of shell have been removed by solution is described. In the table, "diameter" refers to the mean transverse thickness of the drops; ϑ and μ, to the thickness and the mass, respectively, of the dissolved shells. After removing a sufficient depth of shell, the residual explosive properties were tested either by crushing the reduced drop longitudinally in a vice or by striking in the same direction with a hammer.

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[1] De Luynes appears to have been the first to dissolve the drop in HF (C. R. LXXVI, p. 346, 1873). He also discusses elaborately the effects produced by cutting glass with emery (C. R. LXXXI, 341, 1875). Some earlier work on the vacuum bubble is due to Reusch (Phil. Mag. (4), XXXIV, p. 166, 1867).

TABLE V.—*Explosive qualities of Prince Rupert drops.*

No.	Minutes in H. F.	Diameter.	ϑ	μ	Remarks.
		cm.	*cm.*	*g.*	
12	0	0.848	0.006	....	Shattered on breaking base of tail. Explosive tendency diminished in marked degree.
	5	0.835	....	....	
10	0	0.796	0.015	....	Shattered on being split longitudinally. Fragments partially cohere.
	10	0.766	....	....	
11	0	0.795	0.017	....	Shattered on being split longitudinally. Fragments partially cohere.
	14	0.760	....	....	
13	0	0.774	0.031	0.291	Shattered on being split longitudinally. Fragments more coherent.
	30	0.712	....	....	
3	0	0.795	0.054	0.493	Is not shattered on splitting. Conchoidal fracture.
	....	0.688	....	....	
5	0	0.825	0.053	0.491	Is not shattered on splitting. Conchoidal fracture.
	....	0.720	....	....	
7	0	0.763	0.112	0.722	Is not shattered on splitting. Conchoidal fracture.
	....	0.539	....	....	
8	0	0.791	0.117	0.752	Is not shattered on splitting. Conchoidal fracture.
	....	0.557	....	....	

The table shows that the explosive tendency of the Prince Rupert drop becomes rapidly less pronounced as the thickness of removed shell increases, that this tendency is very perceptibly impaired by the removal of less than $\frac{1}{10}^{\mathrm{mm}}$ of shell, and that it vanishes almost wholly after the removal of $\frac{1}{2}^{\mathrm{mm}}$ of shell. If the radius of the drop be diminished about 0.03$^{\mathrm{cm}}$ the particles of the fractured globule frequently cohere, and the original structure may then be inferred from the general direction and distribution of the fissures. The arrangement of the individual fragments is quite characteristic: they are found to be flat, irregular conoids, with their apices toward the line of symmetry of the drop, their bases in its surface—an arrangement something like the eye of an insect, or even more like the fruit cone of a spruce tree. In other words, the radial structure of the fissured Prince Rupert drop is very distinctly marked.[1] This proves that the original (unbroken) drop must have possessed a box-within-box structure; that, if the bubbles were symmetrically disposed, particles similarly situated with reference to the line of symmetry would be in like states of strain. But the law according to which matter is distributed from circumference to axis cannot be inferred, since the stated phenomena follow equally well both for surface dilatation and for surface compression.

All the Prince Rupert drops examined were found to scratch ordinary glass with facility; but, on removing the strain from the drops by annealing them at white heat and slowly cooling them, their hardness

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[1] This structure is frequently visible in fragments of large tempered steel projectiles. I have found glass rods which on sudden heating break up into flat fragments symmetrically disposed around the axis of the rod or again into symmetric conoidal shells (see note on researches of De Luynes, on preceding page).

did not observably change. The hard quality was therefore a property of the glass itself and was not imparted by mechanical treatment. Indeed, on rubbing together a quenched and an annealed Prince Rupert drop no difference of hardness could be discerned.

GENERAL STRUCTURAL EFFECTS PRODUCED BY SUDDEN COOLING.

In Bulletin 35 we communicated a series of results on the resistance of consecutive conaxial layers of steel rods.

We there showed that it is difficult to arrive at accurate values for specific resistance in these measurements, for we encounter very small values of total resistance at the inception of the experiments and small and irregular values of sectional area at the close. Inasmuch as sections are necessarily measured too large, the values for specific resistance, S_0, are too large, and the error increases rapidly as we pass from greater to smaller diameters. The mean error of S_0 is certainly several per cent., and hence the resistances of elementary shells calculated from these data are only approximations. Nevertheless our results are important; they prove that in the case of hard rods less than 0.6^{cm} thick the values of resistance taken from circumference to axis along any radius do not perceptibly diminish. It was this curious result, apparently adverse to the hypothesis of strain, which induced us to examine the corresponding behavior of quenched glass.

The diameters, 2ρ, of Prince Rupert drops Nos. 3, 5, were successively reduced[1] as follows:

	$2\rho = 0.79$	0.75	0.72	0.69	0.62	0.56	cm.,
and	$2\rho = 0.82$	0.79	0.75	0.72	0.65	0.59	cm.

The polarization figures drawn after each of these reductions are subjoined.

The figures of each drop retained a uniform character throughout and showed no further loss of delicacy of demarkation and of colors than could be referred to diminished thickness. Unfortunately it is not easily possible to discriminate between the effect of decrement of diameter and the possibly concomitant effect of lessened birefractive power. Hence the experiments fail to indicate whether the removal of consecutive shells by solution is accompanied by changes of strain (shrinkage). If the fragments of a shattered drop, submerged in glycerine, be examined under the microscope between crossed nicols, the presence of strain in the individual splinters is quite clearly apparent. It is well to note that marked polariscopic evidence of strain remains long after the explosive properties of the Prince Rupert drops have disappeared. We infer that the electrical behavior (resistance) of the successive cores of a hard steel cylinder is not unexemplified by the optical behavior of successive cores of a Prince Rupert drop; though

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[1] We desisted from further reduction of diameter in order not to enter the bubbles.

it is difficult to say whether the behavior of the partial bodies in either case (partial strains) is at all comparable with the behavior of the bodies as a whole (temper strain).

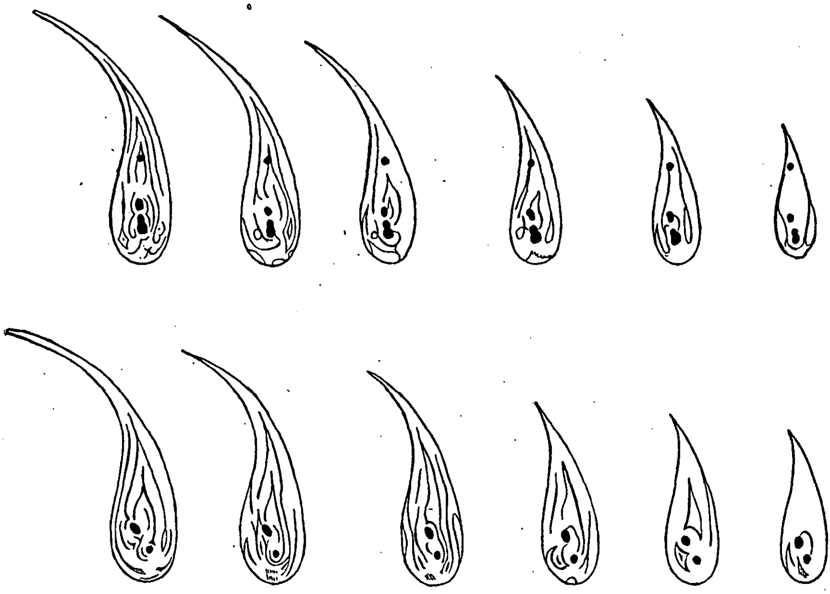

FIG. 9. Polarization figures of successive cores of Prince Rupert drops.

In this place it is well to advert to certain important data of Table IX. Having removed two shells (total thickness, $\vartheta_1+\vartheta_2=0.04^{\mathrm{cm}}$) from each of the Prince Rupert drops Nos. 10 and 11, the core densities were found to be 2.4166 and 2.4147, respectively. We then annealed them in sulphur (450°), and found for the densities of the annealed cores 2.4263 and 2.4261, respectively. This increment is quite as large as is observed when the drops are annealed *as a whole.*[1] Hence we fail to appreciate any diminution of strain due to solution. Moreover, we prove conclusively that the increment of density which is observed on annealing at the said temperature (450°) is a true increment of the density of the substance of the Prince Rupert drop; that is, not a partial collapse of the drop in virtue of atmospheric pressure. In other words, the observed *after action* is inherent in the glass itself, as we pointed out elsewhere.[2]

DISTRIBUTION OF DENSITY IN PRINCE RUPERT DROPS.

Results.—Availing ourselves of the property of the Prince Rupert drop to dissolve quietly in hydrofluoric acid, we arrived at the following results (Tables VI to X) for the variations of density along transverse radii of the drops. In these tables "diameter" denotes the mean

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[1] § I, p. 104.

[2] § I, p. 103.

transverse thickness of the successive cores; M and Δ_t show their mass and their density at the temperature t; Δ_0, their mean density at 0°C. Furthermore, μ, ϑ, δ, R, denote the mass, thickness, density, and mean radius, respectively, of the consecutive shells. If the n^{th} core be left after the removal of n shells, then the suffixes to the number of the drop in the first column give the history of the drop succinctly. Nearly all the measurements are made independently in duplicate. Δ_0 may be relied upon to within two units of the third place; δ, to one unit of the second place. In no case was solution carried so far as to invade the main bubbles of the drops; the drops were chosen as nearly as possible free from small bubbles. The fusions were made in platinum baskets suspended in thick closed clay crucibles. This insured very slow cooling.

TABLE VI.—*Structure of Prince Rupert drops quenched.*

Number.	Diameter.	M	Δ_t	t	Mean Δ_0	μ	ϑ	δ	Mean δ	R
	cm.	*grm.*		°C.		*grm.*	*cm.*			*cm.*
3_0	0.791	1.2577	2.435	15.5	2.4355	......	......	......	......	......
	0.800	1.2576	2.434	16.0	......	......	......	......	......	......
3_1	0.753	1.0375	2.425	16.1	2.4266	0.2202	0.020	2.483	2.478	0.387
	0.756	1.0374	2.426	16.3	......	0.2202	......	2.473	......	......
3_2	0.730	0.8894	2.419	16.7	2.4210	0.1481	0.015	2.461	2.461	0.370
	0.720	0.8893	2.421	16.8	......	0.1481	......	2.461	......	......
3_3	0.698	0.7651	2.411	17.0	2.4120	0.1243	0.019	2.474	2.479	0.353
	0.677	0.7650	2.411	17.3	......	0.1243	......	2.483	......	......
5_0	0.809	1.3002	2.439	15.6	2.4400	......	......	......	......	......
	0.840	1.3000	2.439	15.8	......	......	......	......	......	......
5_1	0.762	1.0924	2.435	16.3	2.4347	0.2078	0.020	2.465	2.469	0.402
	0.810	1.0923	2.434	16.5	......	0.2077	......	2.472	......	......
5_2	0.779	0.9317	2.428	16.5	2.4282	0.1607	0.017	2.477	2.473	0.384
	0.725	0.9318	2.428	16.6	......	0.1605	......	2.470	......	......
5_3	0.703	0.8090	2.418	17.1	2.4181	0.1227	0.016	2.495	2.496	0.368
	0.738	0.8090	2.418	17.4	......	0.1228	......	2.498	......	......

TABLE VII.—*Structure of Prince Rupert drops quenched.*

Number.	Diameter.	M	Δ_t	t	Mean Δ_0	μ	ϑ	δ	Mean δ	R
	cm.	*grm.*		°*C.*		*grm.*	*cm.*			*cm.*
7_0	0.766	1.0897	2.437	17.3	2.4386	......	......	......	......	......
	0.760	1.0897	2.438	18.1	......	......	......	......	......	......
7_1	0.750	1.0035	2.434	18.3	2.4346	0.0862	0.008	2.476	2.485	0.377
	0.743	1.0036	2.433	18.8	......	0.0861	......	2.494	......	......
7_2	0.736	0.9254	2.431	18.6	2.4322	0.0781	0.008	2.468	2.462	0.368
	0.722	0.9254	2.431	18.7	......	0.0782	......	2.455	......	......
7_3	0.718	0.8499	2.428	18.3	2.4288	0.0755	0.008	2.468	2.470	0.360
	0.706	0.8500	2.428	18.9	......	0.0754	......	2.473	......	......
7_4	0.685	0.7363	2.420	19.2	2.4209	0.1136	0.017	2.480	2.482	0.347
	0.672	0.7364	2.419	20.0	......	0.1136	......	2.484	......	......

TABLE VII.—*Structure of Prince Rupert drops quenched*—Continued.

Number.	Diameter.	M	Δ_t	t	Mean Δ_0	μ	ϑ	δ	Mean δ	E
	cm.	*grm.*		°*C.*		*grm.*	*cm.*			*cm.*
7_5	0.647	0.6148	2.410	20.0	2.4098	0.1215	0.018	2.475	2.478	0.329
	0.635	0.6148	2.408	20.2	....	0.1216	....	2.481	....	......
7_6	0.610	0.5136	2.393	19.5	2.3950	0.1012	0.019	2.497	2.489	0.311
	0.597	0.5136	2.394	20.3	....	0.1012	....	2.480	....	......
7_7	0.534	0.3672	2.362	20.2	2.3640	0.1464	0.032	2.477	2.476	0.285
	0.544	0.3672	2.363	20.6	....	0.1464	....	2.475	....	......
8_0	0.781	1.1422	2.439	17.5	2.4396	....	....	....	....	......
	0.800	1.1422	2.438	18.0	....	....	....	....	....	......
8_1	0.766	1.0567	2.436	18.4	2.4372	0.0855	0.007	2.477	2.469	0.391
	0.783	1.0567	2.436	18.6	....	0.0855	....	2.461	....	......
8_2	0.765	0.9739	2.432	18.7	2.4344	0.0828	0.010	2.477	2.471	0.382
	0.745	0.9739	2.434	18.6	....	0.0828	....	2.465	....	......
8_3	0.745	0.9024	2.431	18.5	2.4317	0.0715	0.008	2.455	2.469	0.373
	0.730	0.9024	2.430	19.0	....	0.0715	....	2.483	....	......
8_4	0.713	0.7741	2.421	19.3	2.4225	0.1283	0.016	2.489	2.489	0.361
	0.696	0.7741	2.421	19.8	....	0.1283	....	2.489	....	......
8_5	0.675	0.6567	2.412	20.2	2.4129	0.1174	0.019	2.479	2.478	0.343
	0.659	0.6567	2.412	20.2	....	0.1174	....	2.476	....	......
8_6	0.623	0.5459	2.403	19.7	2.4042	0.1108	0.018	2.454	2.457	0.324
	0.636	0.5460	2.402	20.2	....	0.1107	....	2.460	....	......
8_7	0.565	0.3901	2.373	20.4	2.3743	0.1558	0.036	2.485	2.483	0.297
	0.550	0.3901	2.373	20.5	....	0.1559	....	2.480	....	......
9_0	0.761	1.0518	2.4377	17.6	2.4390	....	....	....	....	......
	0.757	1.0517	2.438	17.8	....	....	....	....	....	......
9_1	0.746	0.9638	2.436	18.5	2.4370	0.0880	0.007	2.455	2.460	0.375
	0.742	0.9638	2.436	18.6	....	0.0879	....	2.465	....	......
9_2	0.720	0.8689	2.432	18.8	2.4338	0.0949	0.010	2.475	2.467	0.366
	0.726	0.8689	2.433	18.5	....	0.0949	....	2.459	....	......
9_3	0.711	0.7981	2.429	18.6	2.4302	0.0708	0.008	2.466	2.475	0.357
	0.703	0.7981	2.429	18.8	....	0.0708	....	2.483	....	......
9_4	0.683	0.6932	2.423	19.5	2.4238	0.1049	0.016	2.473	2.474	0.345
	0.667	0.6931	2.422	19.6	....	0.1050	....	2.474	....	......
9_5	0.628	0.5846	2.415	20.2	2.4161	0.1086	0.019	2.469	2.466	0.327
	0.644	0.5845	2.415	20.2	....	0.1086	....	2.463	....	......
9_6	0.613	0.4867	2.406	19.8	2.4064	0.0979	0.018	2.458	2.465	0.308
	0.585	0.4866	2.404	20.2	....	0.0979	....	2.473	....	......
9_7	0.548	0.3471	2.375	20.5	2.3765	0.1396	0.031	2.488	2.484	0.283
	0.524	0.3471	2.375	20.5	....	0.1395	....	2.481	....	......

The following densities were found for glass very slowly cooled from fusion:

No.	7_7	8_7	9_7
M	0.3102	0.3424	0.2779
Δ_0	2.495	2.498	2.501

Table VIII, constructed on the plan described for Tables VI and VII, contains results for the variation of density along the transverse axis of drops annealed in boiling sulphur at 450°. Polariscopic observation showed these drops to be free from strain.

TABLE VIII.—*Structure of Prince Rupert drops annealed at* 450°.

No.	Diameter.	M	Δt	t	Mean Δ_0	μ	ϑ	δ	Mean δ	R
	cm.	*grm.*		°C.		*grm.*	*cm.*			*cm.*
1_0	0.766	1.1663	2.439	19.0	2.4398	....	....	....	....	......
	0.768	1.1662	2.439	19.0	....	....	....	....	....	......
1_1	0.708	0.8897	2.424	17.0	2.4242	0.2766	0.028	2.489	2.491	0.369
	0.713	0.8897	2.423	17.4	....	0.2765	....	2.493	....	......
1_2	0.685	0.7859	2.414	17.4	2.4147	0.1038	0.011	2.503	2.503	0.350
	0.690	....	....	......	....	....	....	....	....	......
2_0	0.980	1.8913	2.441	19.0	2.4420	....	....	....	....	......
	0.884	1.8914	2.441	19.2	....	....	....	....	....	......
2_1	0.920	1.4791	2.429	17.4	2.4303	0.4122	0.029	2.488	2.484	0.451
	0.828	1.4790	2.430	17.4	....	0.4124	....	2.481	....	......
2_2	0.798	1.3118	2.422	17.4	2.4231	0.1673	0.021	2.484	2.484	0.426
	0.866	....	....	......	....	....	....	....	....	......
6_0	0.792	1.2048	2.446	19.0	2.4468	....	....	....	....	......
	0.797	1.2048	2.446	19.0	....	....	....	....	....	......
6_1	0.743	0.9329	2.434	17.2	2.4350	0.2719	0.027	2.487	2.488	0.384
	0.738	0.9329	2.434	17.4	....	0.2719	....	2.490	....	......
6_2	0.707	0.8436	2.4274	17.4	2.4284	0.0893	0.015	2.504	2.504	0.362
	0.712	....	....	......	....	....	....	....	....	......

In Table IX, finally, we give the results for the Prince Rupert drops Nos. 10 and 11. The first two shells were removed from the drops while in the original (quenched) state. Both were then annealed for two hours at 450° and a further removal of shell effected. The numbers referring to the annealed state are primed. In other respects the notation is that of the preceding tables.

TABLE IX.—*Structure of Prince Rupert drops.*

No.	Diameter.	M	Δ_t	t	Mean Δ_0	μ	ϑ	δ	R	Remarks.
	cm.	*g.*		°*C.*		*g.*	*cm.*		*cm.*	
10_0	....	1.2984	2.4333	21.5	2.4346	....	....	....	....	Quenched.
	....	1.2985	2.4331	21.9	....	....	....	....	....	
10_1	0.775	1.0766	2.4260	22.0	2.4269	0.2218	(0.02)	2.471	(0.39)	
	0.747	1.0767	2.4250	22.2	....	0.2218	....	2.475	....	
10_2	0.735	0.9014	2.4147	21.3	2.4166	0.1732	0.022	2.487	0.370	
	0.699	0.9014	2.4160	21.5	....	0.1733	....	2.475	....	
$10'_2$	0.733	0.9014	2.4253	22.0	2.4263	....	....	....	....	Annealed at 450°, 2h.
	0.700	0.9014	2.4246	22.2	....	....	....	....	....	
$10'_3$	0.697	0.7425	2.4127	22.0	2.4136	0.1589	0.020	2.488	0.348	
	0.654	0.7425	2.4118	22.3	....	0.1589	....	2.488	....	
$10'_4$	0.656	0.6133	2.3958	22.4	2.3982	0.1292	0.020	2.498	0.328	
	0.617	0.6132	2.3978	21.5	....	0.1293	....	2.482	....	

TABLE IX.—*Structure of Prince Rupert drops.*—Continued.

No.	Diameter.	M	Δ_t	t	Mean Δ_0	μ	ϑ	δ	R	Remarks.
	cm.	*g.*		°*C.*		*g.*	*cm.*		*cm.*	
11_0	....	1.0470	2.4350	21.6	2.4357	....	....	....	....	Quenched.
	....	1.0457	2.4337	21.7	....	....	....	....	....	
11_1	0.730	0.8555	2.4271	22.0	2.4281	0.1915	(0.02)	2.473	(0.37)	
	0.707	0.8555	2.4263	22.2	....	0.1902	....	2.469	....	
11_2	0.690	0.7173	2.4138	21.5	2.4147	0.1382	0.020	2.500	0.350	
	0.670	0.7173	2.4131	21.6	....	0.1382	....	2.499	....	
$11'_2$	0.690	0.7172	2.4245	22.0	2.4261	....	....	....	....	Annealed at 450°, 2^h.
	0.670	0.7173	2.4249	22.0	....	....	....	....	....	
$11'_3$	0.626	0.5825	2.4077	22.1	2.4086	0.1347	0.023	2.502	0.329	
	0.644	0.5825	2.4067	22.2	....	0.1348	....	2.508	....	
$11'_4$	0.603	0.4678	2.3894	22.5	2.3919	0.1147	0.023	2.487	0.306	
	0.578	0.4677	2.3917	21.6	....	0.1148	....	2.471	....	

Discussion.—An inspection of Tables VI and VII shows at once that Δ_0, the density of consecutive cores, continually decreases. This is easily accounted for, since the bubble error becomes relatively large as the mass (M) of the Prince Rupert drop decreases.

If we construct the density of consecutive shells (δ) as a function of their mean radius (R) and then compare the diagrams which obtain for the five Prince Rupert drops, Nos. 3, 5, 7, 8, 9, we find that the loci have no salient feature in common. Possibly an increase of δ as we approach the deeper layers may be discernible, but it is indistinct. Hence the true variation of δ from surface to axis of a Prince Rupert drop is here unrecognizably obscured by errors of observation. Indeed, we shall find below that the probable total variation of δ attributable to strain will not far exceed 0.5 per cent. The accuracy of δ is certainly not within this figure. Again, if we compare the contours of corresponding curves $\delta = f(R)$, in Table V for drops free from strain, with each other and with the contours belonging to Tables III and IV, we encounter fluctuations of the same kind in both cases. These errors include the inaccuracies of mere measurement (the mass of the drops is unfortunately small and the pycnometer methods are not easily applicable), as well as such discrepancies as result from the unavoidable invasion of small bubbles during solution.

If, however, we compare the *mean* values of δ for strained shells (Tables VI, VII, and IX) with the mean values of δ for shells free from strain (Tables VII and IX), we find the latter values (unstrained glass) always in excess of the former. In other words, although our results are insufficiently sharp to enable us to describe the exact nature of the temper strain in glass, they do permit us to classify it as a *strain of dilatation*, so far as we have observed, throughout the substance of the drop. This observation is of importance, and we have therefore drawn up the following general tabular comparison, to supplement the special and direct comparison given in Table IX.

In Table X Δ_s is the density of the glass itself after thorough annealing at red heat, as found in our earlier section, page 117, the datum being the mean value for six drops; Δ'_s is the density of the glass after *fusion* in a platinum basket and very slow cooling. The additional increment of the density of the glass thus produced is to be noted. δ_h and δ' denote the densities of shells strained (quenched) and unstrained (annealed at 450°), respectively. The sixth column contains the relative value of decrement of density for each drop; the second column, finally, the number of shells whose average δ is the datum given.

TABLE X.—*Density relations of tempered glass relative to soft glass (mean results for shells).*

$\Delta_s = 2.491$			$-\frac{\delta' - \Delta_s}{\Delta_s} = 0$		
Prince Rupert drop No. —	Number of shells dissolved.	δ_h	′	Δ'_s	$-\frac{\delta_h - \delta'}{\Delta_s}$
3	3	2.473 ± 0.006			0.0076
5	3	2.479 ± 0.008			0.0052
7	7	2.477 ± 0.003		2.495	0.0060
8	7	2.474 ± 0.004		2.498	0.0072
9	7	2.470 ± 0.003		2.501	0.0088
10	2+2	2.477 ± 0.008	2.489 ± 0.002		0.0064
11*a*	2+2	2.485 ± 0.029	2.492 ± 0.026		0.0028
1	2		2.497 ± 0.006		
2	2		2.484 ± 0.000		
6	2		2.496 ± 0.008		
Mean	$(\frac{41}{10})$	2.476	2.492	2.498	0.0063

a In view of the large value of probable mean error of this measurement, we thought seriously of rejecting it; but we were unable to find any error in the work, and hence the datum has been retained. Its effect is principally apparent in the ratio, which it depresses in a way adverse to our inferences.

To facilitate further comparison, we insert also the corresponding table for steel.[1] Here 2 ρ are the diameters of the steel rods; Δ_h, Δ_s, Δ_c, their densities in the hard, the soft, and the commercial soft states, respectively. Δ', finally, denotes the observed densities of steel at the end of the first phase of annealing (350°), and therefore applies for rods free from æolotropic strain. The table gives us the following relative decrements of density: column first, the total decrement; columns second and third, the decrements corresponding to the first and second phases of annealing, respectively.

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[1] See Bull. No. 27, U. S. Geol. Surv., p. 46.

TABLE XI.—*Density variations of tempered steel relative to soft steel.*

No.	2ρ	$-\frac{\Delta_h-\Delta_s}{\Delta_c}$	$-\frac{\Delta_h-\Delta'}{\Delta_c}$	$-\frac{\Delta'-\Delta_s}{\Delta^c}$
I	1.90	0.0048	0.0018	0.0029
II	0.58	0.0155	0.0060	0.0095
61 to 63....	0.13	0.0171	0.0068	0.0103
0...........	0.23	0.0133	0.0080	0.0053
21 to 29....	0.08	0.0150	0.0033	0.0116
Mean ...	......	0.0131	0.0052	0.0079

Tables X and XI show that both in the case of glass and of steel the mean strain effect of sudden cooling is *dilatation* throughout the mass of the quenched material,[1] that the mean amounts of dilatation for glass and for steel are of like order, and that the strain in glass exceeds that of steel. We find, in general, that the practically measurable value of density is not a satisfactorily sharp datum for discerning the primary causes of the electrical, the optic, and the magnetic variations of the substance quenched. These, therefore, will have to furnish nice descriptions of strain and interpret what we have called elsewhere the individuality of magnets.

In the above paragraphs we have pursued the analogy between the optical behavior of tempered glass and the electrical behavior of tempered steel into every detail of consideration which urged itself. We availed ourselves, moreover, of additional criteria given by the density relations of the whole or of similar parts of the bodies quenched. At every stage of our work we reached data alike in character both for steel and for glass. With these results we are further justified in maintaining that sudden cooling of steel is accompanied by a strain effect of a distinct and individual kind and of an intensity sufficient to account for the electrical properties of steel (thermo-electric and resistance constants) such as we have found them.

In one of the earlier paragraphs of the present paper we pointed out that in its divers relations to hardness steel is distinguished from glass. To further our investigation it will therefore next be necessary to inquire more specifically into the causes of hardness itself, and at the same time to endeavor to throw light on the mysterious transformations of carbon.

§ III. THE HYDRO-ELECTRIC EFFECT OF TEMPER.

Our original object in writing these papers was that of elucidating questions having reference to the carburation of steel, from a purely physical standpoint. The reasoning available to the physicist is, however, of an analogical kind, and therefore as dangerous as it is fascinating. Hence, in view of the time already spent, it seemed expedient to en-

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[1] If "quenching" means sudden cooling, then if the solid quenched be massive and thick the deep layers cannot be quenched in virtue of their position.

deavor to cut more nearly down into the heart of the inquiry and to determine directly the carbon relations of steel as a function of the temperature (0° to 400°, 400° to 1000°) and of the time of annealing, and to do this with full reference to the physical occurrences observed in the first and second phases of the phenomenon. So far as we know, M. Caron[1] alone has occupied himself with similar work; but his researches, being largely restricted to the extreme states "hard" and "soft," are incomplete. The carburation effect of annealing at measured temperatures during stated times is quite unknown.

Glass hard steel rods about 0.1^{cm} in diameter and tempered uniformly in the way described elsewhere[2] were each broken into four nearly equal parts and four samples of hard steel identical in composition and temper were thus obtained. These samples were annealed at 20° (glass hard), 100° 4^h, 200° 1^h, 360° 1^h, 1000° 5^m, respectively. Having treated these with cold dilute hydrochloric acid, we found that the rods annealed at 20° and at 100° dissolved without perceptible residue to a clear liquid; those annealed at 200° left a trace of flocculent carbon. Rods annealed at 360° yielded flocculent carbon in considerable amount; rods annealed at 1000°, finally, a comparatively copious and heavy carbon precipitate. The residues were collected in a weighed Gooch crucible (asbestus filter), thoroughly washed in the usual way,[3] dried, weighed, ignited in oxygen, again weighed, and the loss of weight on ignition estimated as carbon. The results thus obtained are sufficient for the present purposes:

Annealed at	$20°, \infty$	$100°, 4^h$	$200°, 1^h$	$360°, 1^h$	$1000°, 5^m$
Uncombined (graphitic) carbon per gramme steel, c.	<0.0007	<0.0007	0.0009	0.0021	0.0047

In a second series of similar experiments we found—

Annealed at	$20°, \infty$	$100°, 10^h$	$200°, 1^h$	$360°, 1^h$	$450°, 1^h$	$1000°, 30^m$	Commercial (soft).
Uncombined (graphitic) carbon per gramme steel, c.	0.0001	0.0005	0.0005	0.0014	0.0009	0.0033	0.0053

In general, c increases at an accelerated rate with temperature. The large datum for the commercial state, as compared with the smaller values of c for steel softened by mere heating to redness, is an interesting feature of these results. The importance of the time effect is also to be noted. Temperatures as low as 100°, when acting on hard steel for long intervals of time (10^h), produce perceptible precipitation of the carbon in steel.

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[1] Caron: Comptes-rend., LVI, pp. 43, 211, 325, 1863.

[2] Bull. 14, U. S. Geol. Surv., p. 29, 1885; Bull. 27, U. S. Geol. Surv., p. 30, 1886.

[3] Using dilute HCl, hot water, solution KOH, alcohol, and ether. See Blair: Report of the Board on Testing Iron, &c., I, p. 248. Washington, 1881.

On closer inspection it appeared that steel annealed at 100° is, cæteris paribus, more easily soluble than glass hard steel; steel annealed at 200° more easily soluble than steel annealed at 100°, and steel annealed at 360° more easily soluble than steel annealed at 200°. In other words, the rate at which solution takes place in general increases as temper continually decreases. These curious results were substantiated by annealing one-half of short glass hard rods (ca. 5^{cm} in length) at red heat on dissolving in HCl, the diameter of the soft length is diminished more rapidly than the diameter of the hard length. The diminution is usually greatest near the middle of the rod, where hard and soft parts meet, showing probably that local galvanic action here produces a perceptible result. At the same time steel annealed for hardness at a temperature in low redness is probably more soluble than steel in any other state of temper, hard or soft. Examples are given in the next table.

If we define the rate of solution as the mass dissolved per unit of area per unit of time, then in case of two submerged cylinders, for which during the time t the radii are reduced from ρ_0 to ρ and from ρ_0 to ρ', respectively, the rates, cæteris paribus, will be to each other as corresponding values of the expression—

$$-\delta\int_{\rho_0}^{\rho}\frac{2\pi\rho d\rho}{2\pi\rho}, \text{ or as } \frac{\rho_0-\rho}{\rho_0-\rho'}$$

The following table contains some of the results obtained with rods in the hard (h) and the soft (s) states, respectively, dissolved in acid, HCl, under identical conditions. m refers to the middle parts of the rods, concerning which mention has already been made. These ratios are subject, of course, to large variations (1 to 20), depending on the method of annealing, &c. The table is a fair exhibit of average values. The rods are lettered A, B, C, D.

TABLE XII.—*Rates of solution of hard and soft steel.*

[Original diameter, $2\rho_0 = 0.120^{cm}$.]

	Diameter.				Rates.				
	A.	B.	C.	D.	A.	B.	C.	D.	Mean rate.
h	0.111	0.111	0.110	0.110	1.0	1.0	1.0	1.0	1.0
m	0.101	0.100	0.098	0.100	1.7	1.7	1.8	1.6	1.7
s	0.102	0.103	0.102	0.103	1.6	1.5	1.5	1.4	1.5
h	0.101	0.100	0.100	0.099	1.0	1.0	1.0	1.0	1.0
m	0.080	0.084	0.083	0.081	1.7	1.6	1.6	1.7	1.6
s	0.094	0.092	0.091	0.090	1.3	1.3	1.3	1.3	1.3
h	0.069	0.071	0.073	0.072	1.0	1.0	1.0	1.0	1.0
m	0.045	0.045	0.043	0.044	1.4	1.5	1.6	1.5	1.5
s	0.067	0.070	0.070	0.071	1.0	1.0	1.0	1.0	1.0

TABLE XII.—*Rates of solution of hard and soft steel*—Continued.

[Original diameter, $2\rho_0 = 0.126^{cm}$.]

	Diameter.				Rates.				
	A.	B.	C.	D.	A.	B.	C.	D.	Mean rate.
h	0.122	0.123	0.122	0.122	1.0	1.0	1.0	1.0	1.0
s	0.115	0.116	0.115	0.113	2.7	3.3	2.8	3.2	3.0
h	0.116	0.116	0.116	0.115	1.0	1.0	1.0	1.0	1.0
s	0.103	0.108	0.106	0.104	2.3	1.8	2.0	2.0	2.0
h	0.090	0.090	0.089	0.090	1.0	1.0	1.0	1.0	1.0
s	0.052	0.061	0.052	0.058	2.0	1.8	2.0	1.9	1.9
h	0.078	0.077	0.077	0.076	1.0	1.0	1.0	1.0	1.0
s	0.038	0.029	0.028	0.042	1.8	2.0	2.0	1.7	1.9

[Original diameter, $2\rho_0 = 0.082^{cm}$.]

h	0.077	0.077	0.078	0.076	1.0	1.0	1.0	1.0	1.0
s	0.070	0.065	0.066	0.068	2.4	3.4	4.0	2.3	3.0
h	0.070	0.070	0.070	0.070	1.0	1.0	1.0	1.0	1.0
s	0.060	0.051	0.059	0.051	1.8	2.6	1.9	2.6	2.2
h	0.043	0.041	0.044	0.043	1.0	1.0	1.0	1.0	1.0
s	0.000	0.000	0.000	0.000	2.1	2.0	2.1	2.1	2.1

From these results we inferred that hard and tempered steel would probably be distinguishable hydro-electrically; that, for the first phase of the phenomena of annealing, at least, this distinction might be more delicate than the estimation of precipitated carbon. To test this inference we selected the rods Nos. 1 to 12, quenched uniformly glass hard by our method. These were then broken in the middle and the first half of each rod was left in the glass hard state. The other halves were annealed in pairs at 20°, 100°, 4^h, 185°, 360°, 450°, 1000°, respectively. In order to anneal these (long) rods uniformly, we used a special device by which they were drawn vertically upward through a zone of constant temperature by clock work. If h be the height of this zone and ρ the radius of the disk or drum revolving once an hour, then

$$t = \frac{h}{2\pi\rho}$$

is the time of annealing in hours. Again, if we make $h = 2\pi$, then the time of exposure in hours is the reciprocal of the radius of the disk in centimeters. The great advantage of this method of annealing is that it requires but a very *small* zone of constant temperature;[1] it is therefore applicable at all temperatures and almost invaluable for high temperature work (500° to 1500°), where zones of a definite constant temperature are not easily produced. In this way we obtained six *pairs* of hydro-electric couples, each of which consisted of glass hard steel and the same steel annealed at one of the temperatures specified. Our first results were investigated with a zero method, and showed clearly that

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[1] $2\pi \times \pi (0.3)\ \overline{\mathrm{cm}}^{3}$ or even a narrower cylindrical figure being sufficient.

annealed steel is hydro-electrically positive with reference to hard steel and that the electromotive force increases with the difference of temper. But in view of the large polarization discrepancies incident to these measurements, the electrometer is preferable to the zero instrument. The following results were obtained with Mascart's apparatus adjusted to indicate 0.001 volt accurately. The electrodes of the steel couple were immersed in a concentrated solution of pure zinc sulphate contained in a U tube, the two limbs of the tube receiving the two steel wires. We kept them scrupulously bright by repeated scouring with sand paper. In the tables we give the electromotive forces, *e*, of the divers couples of hard and tempered steel, as well as the probable mean error, δe, of each. The means of the two values of *e* for each temperature of annealing are given in the second horizontal row and fairly exhibit the hydro-electric effect of temper in question.

The following data are the mean results of four sets of measurements of five observations per set. The rods were scoured before beginning the first and the third of these sets.

	No.	$e \times 10^3$	$\delta e \times 10^3$	Mean $e \times 10^3$
Annealed at 20°	9	± 4	....	±0.009
	10	±13	....	
Annealed at 100°	1	+12	±4	+0.000
	2	− 2	±5	
Annealed at 190°	3	+19	±3	+0.020
	4	+20	±1	
Annealed at 360°	5	+36	±3	+0.035
	6	+34	±3	
Annealed at 450°	7	+35	±3	+0.037
	8	+40	±3	
Annealed at 1000°	11	+49	±4	+0.052
	12	+54	±4	

The following data are the mean results of four sets of five observations per set; rods scoured before commencing each set of measurements:

	No.	$e \times 10^3$	$\delta e \times 10^3$	Mean $e \times 10^3$
Annealed at 20°	9	± 5	....	±0.003
	10	± 2	....	
Annealed at 100°	1	+ 8	±3	+0.007
	2	+ 7	±1	
Annealed at 190°	3	+20	±3	+0.022
	4	+24	±2	
Annealed at 360°	5	+34	±5	+0.030
	6	+27	±1	
Annealed at 450°	7	+35	±2	+0.039
	8	+43	±2	
Annealed at 1000°	11	+51	±2	+0.058
	12	+65	±5	

The following data, finally, are the mean results of two sets of three observations per set; rods scoured before commencing each set of measurements:

	No.	$e \times 10^3$	$\delta e \times 10^3$	Mean $e \times 10^3$
Annealed at 20°	9	± 2	....	±0.003
	10	± 4	....	
Annealed at 100°	1	+ 6	±2	+0.006
	2	+ 6	±1	
Annealed at 190°	3	+16	±3	+0.021
	4	+25	±1	
Annealed at 360°	5	+36	±2	+0.035
	6	+34	±1	
Annealed at 450°	7	+37	±2	+0.038
	8	+39	±2	
Annealed at 1,000°	11	+59	±6	+0.062
	12	+65	±8	

The electromotive forces here encountered are small. It is necessary to take extreme precautions against all sources of error; otherwise mere discrepancies of polarization will exceed the largest values of electromotive force (*e*) found. If the parts of the liquid in which the steel wires are immersed differ at all in composition we may look for a difference of potential at the surface of separation of those parts. The number of such surfaces in a solution of solid liquid or gas may be indefinite. Hence it appeared desirable to repeat the above experiments with distilled water in place of zinc sulphate, to exchange the limbs of the U tube twice for each series of measurements (commutation), and to submerge equal surfaces of steel electrode in all cases. The results follow:

	No.	$e \times 10^3$	$\delta e \times 10^3$.	Mean $e \times 10^3$
Annealed at 0°	9	± 18	....	±0.023
	10	± 28	....	
Annealed at 100°	1	+ 12	± 5	+0.020
	2	+ 28	± 9	
Annealed at 190°	3	+ 33	± 7	+0.027
	4	+ 20	± 8	
Annealed at 360°	5	+ 93	±11	+0.089
	6	+ 85	± 6	
Annealed at 450°	7	+128	±15	+0.105
	8	+ 82	± 9	
Annealed at 1000°	11	+166	± 5	+0.185
	12	+205	± 3	

A few supplementary data are contained in the next table, where Nos. I and II are (+) iron /(—) steel couples, both metals in the soft state; No. III, a couple of nominally identical iron wires; Nos. IV and V, couples consisting of steel in the commercial, drawn state (+), and the same steel softened by heating to redness (—). The couples are immersed in water.

I.	II.	III.	IV.	V.
$e \times 10^3$	$e \times 10^3$	$e \times 10^3$	$e \times 10^3$	$e \times 10^3$
$+26 \pm 3$	$+63 \pm 2$	± 20	-69 ± 5	-65 ± 12

The general results of these measurements are in accordance; the variations of potential, when taken as a whole, regular and decided. They show that *as hardness increases the hydro-electric position of steel moves continually in an electro-negative direction.* The electromotive forces encountered are larger for the electrolyte distilled water than for zinc sulphate. The total range of variation in the former case (water) may exceed 0.25 volt. For zinc sulphate it scarcely reaches one-third of this amount and decreases as the time of immersion increases. After the first immersion, moreover, the original electromotive force is not fully restored even by rubbing the electrodes.[1] When steel is immersed in water the effect of repeated scouring seemed to be an increase of electromotive force. But these and like annoyances, which make the study of polarization phenomena unsatisfactory, are too well known to need further comment here.

If we avail ourselves of the observations made above on the rate of solution of tempered steel, we may infer consistently with all the facts adduced that, since the tempered electrode is covered with hydrogen[2] at a greater rate than the hard electrode, the former must be positive with respect to the other; that the phenomena in hand are mere effects of polarization. In other words it is permissible to assume that the continuous variation of mechanical texture producible by annealing is the cause of corresponding variations of the rate at which hydrogen is deposited on the submerged metal; that the electromotive forces observed are expressions of this hydrogen polarization and bear no immediate relation to the electro-chemical character of the steel electrode.

On the other hand the dependence of the hydro-electric position of steel, cæteris paribus, on the amount of free carbon contained is sufficiently obvious to conflict with this view. To facilitate comparison we insert the following table. Here c denotes the number of grammes of free carbon per gramme of steel; e and e' show the difference of potential between steel tempered and steel hard when plunged in zinc sulphate and in water, respectively; Δ is the density, s the specific resistance, α the

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[1] After long exposure of the wires to air the original electro motive force again appears.

[2] Hydrogen accumulates visibly on the + electrode when both are immersed in zinc sulphate.

resistance temperature coefficient, h the thermo-electric hardness of wires of the same kind of steel. α and h are obtained by calculation.

TABLE XIII.

[Diameter, $2\rho=0.081$.]

Annealed from hard at—	c	e	Δ	s	α	h	e'
20° ∞	0.0001	0.000	7.6547	43.9	0.0017	18.1	0.000
100, 1^{h}........	....	....	7.6666	39.3	0.0018	16.2	....
100, 13^{h}.......	0.0005	0.006	7.6745	35.5	0.0020	14.6	0.020
190, 4^{h}........	....	....	7.6841	30.8	0.0023	12.7	....
190, 4^{h}, 30^{m}....	....	....	7.6808	27.1	0.0027	11.2	....
Do.........	0.0007	0.020	7.6848	27.1	0.0027	11.2	0.027
350............	0.0017	0.033	7.6806	20.7	0.0033	8.5	0.089
450, 1^{h}........	0.0009	0.038	7.7190	18.4	0.0036	7.6	0.105
530............	....	....	7.7227	18.2	0.0036	7.5	....
690............	....	....	7.7272	17.2	0.0038	7.1	....
810...........	....	....	7.7586	17.6	0.0037	....	....
1,000.........	0.0040	0.057	7.7705	18.6	0.0037	....	0.185
Commercial..	0.0053	....	7.7268	16.3	0.0039	6.7	0.252

When steel of a given kind is operated upon, and total carbon therefore a fixed quantity, the variable c affords a comparatively convenient means for detecting the presence and amount of chemical change; but it is highly probable that a much clearer insight into the nature of the decomposition of carbide produced by annealing hard steel would be obtainable from a study of the character and quantity of the hydrocarbons[1] (gaseous liquid) volatilized during solution. They accumulate in copious amounts long before the precipitation of carbon is perceptible, or even when no appreciable precipitation occurs. If we regard c and e or e' correlated, then we have in hand an example of an exceedingly remarkable decomposition, which may be regarded as incipient in hard steel even at ordinary temperatures, which is a certainly perceptible occurrence after annealing at only 100°, and which becomes more and more definitely marked and distinct as the temperature and time of annealing increase. The anomalous character of this species of decomposition, when occurring in a rigid solid, we have already fully pointed out. To obtain further information it is essential that the variable c be investigated minutely. We remark that the critical difference between the thermo-electric (h) and the hydro-electric (c) behavior of steel is well shown by constructing h as a function of e'. This is done in figure 10, which also contains c in its relations to e'.

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[1] The liquid and volatile constituents seem to increase in amount as the steel dissolved is harder.

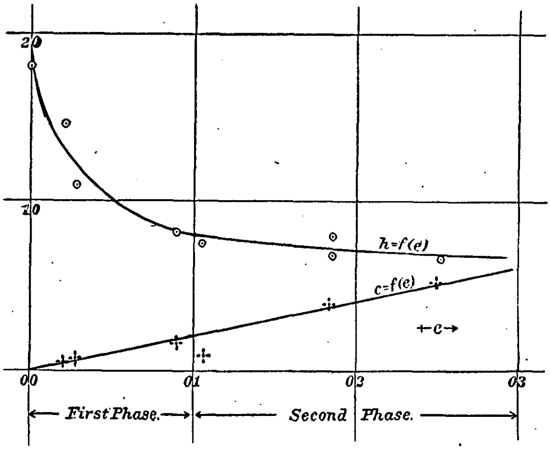

FIG. 10. Diagram illustrating the relation of graphitic carbon and thermo-electric hardness to the hydro-electric position of steel.

RETROSPECTIVE REMARKS.

The present results have materially substantiated our earlier views at every essential point. We may, nevertheless, further point out the presence and the importance of the strain effect by the following simple considerations:

The mass constants of the three types of cast iron, the extreme gray, the intermediate mottled, and the extreme white, range between the maximum density of 7.6 for white cast iron and the minimum density of 6.9 for gray cast iron. Density, therefore, *increases* in marked degree in proportion as total carbon is more and more nearly combined (from "gray" to "white"). Quite the reverse of this is true for steel, where density decidedly *decreases* as total carbon is more and more nearly combined (from soft to hard). This discrepancy is the temper strain, a strain of dilatation, which, in Chapters I and II, we carefully compare with the analogous behavior of glass. It is to be remembered that the given differences of density apply even to parts of the *same* cast of iron,[1] when these parts are respectively cooled rapidly (white) or slowly (gray).

With these general indications of the occurrence of stress, it is an important desideratum to obtain some estimate of its value. One method premises that the work done in mechanically expanding steel or glass from normal density to quenched density is equivalent to the work done by heat in effecting the same expansion. Here we have

$$\int p\,dv = A\,c\,T$$

where in one case unit of mass is acted on by a force p dynes per square centimeter during the volume increase dv cubic centimeters; where, in the other case, an identical total volume increment $(\int dv)$ is produced

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[1] Karsten: Eisenhüttenkunde, Bd. I, 3. Aufl., p. 581 ff, 1841.

by an excess of temperature T degrees centigrade, applied to the same unit of mass and of mean specific heat c. A is Joule's equivalent. If, instead of variable p, we employ a mean constant value, P, and put for T the thermal value $\frac{1}{3\alpha}\int dv$,

We find

$$P=A\,\frac{c}{3\alpha}$$

Here

$$A=42\times 10^6,\ c=0.2,\ 3\alpha=25\times 10^{-6}$$

hence we obtain

$$P=320\times 10^9$$

dynes per square centimeter, or circa 300,000 atmospheres. This is an absurdly large value and shows that in case of thermal expansion internal work is done which is not registered in mere volume increase.

We obtain very plausible stress values by introducing the elastic properties of glass or steel, probably because we are here relatively free from hypotheses. The compression (negative expansion) produced by quenching glass or steel is given in Tables X and XI, § II, and may be accepted as 5×10^{-3}. The volume resilience of glass and of steel, according to Professor Everett's[1] measurements, is 4×10^{11} and 2×10^{12}, respectively. Hence, if the force resisted in producing the volume increment of quenching be equivalent to the force producing the identical compression, we find $P=10\times 10^9$ dynes per square centimeter for steel and $P=2\times 10^9$ for glass. Now, the tenacity of steel is 8×10^9 per square centimeter; the tenacity of glass, 0.6×10^9 per square centimeter. The ratio of stress to tenacity is therefore 1.3 for steel and 3.3 for glass. This shows that in both cases stress and tenacity are of the same order, and that stress is in excess, and but for the peculiarly favorable and resisting arched structure of the quenched globule would give rise to rupture — in glass certainly, very probably also in steel. These results are estimates and are in accord with the observed explosive property of the Prince Rupert drop, and with the less pronounced tendency of steel to crack on quenching. We may infer, therefore, that quenched glass and quenched steel are under mean stress intensities of several thousand atmospheres; and in discussing the corresponding viscous properties of these substances they must be brought into relation with these high intensities of peculiar stress.

We call attention, in concluding, to the deductions of our earlier paper: "The annealing of steel, considered physically, is at once referable to the category of viscous phenomena. In the ordinary cases of viscosity measurements the phenomenon is evoked by sudden application of stress (torsion, flexure, tension, volume compression, &c.) under conditions of constant viscosity; in the case of annealing, by sudden de-

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[1] Everett: Phil. Trans., p. 369, 1867. The above are round numbers.

crease of viscosity under conditions of initially constant stress. Thermal expansion interferes with the purity of these phenomena by destroying the conditions of existence of the strain which accompanies hardness, and this in proportion as the expansion is greater."[1]

Again, irrespective of the manifestation of mere hardness: "The existence of the characteristic strain in glass hard steel is the cause of electrical effects so enormous that such additional effects which any change of carburation may involve may be disregarded, and all electrical and magnetic results interpreted as due to variations in the intensity of the said strain."[2]

This deduction applies of course to the first phase of the phenomena of annealing, since it is within these limits that the strain in question is brought to vanish. With these results in hand we may proceed justifiably toward a study of the question whether the conditions for the permanent retention of magnetism in an iron carburet are not the identical conditions for the permanent retention of any strain. If we select the temper strain for comparison, we do it not merely because long experience has familiarized us with this strain, but because of the clear cut beauty of its manifestations and because of the simplicity of the functions which describe it.

WASHINGTON, *September*, 1886.

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[1] Bull. 14, U. S. Geol. Surv., p. 196.

[2] Id., p. 197.

THE SPECIFIC GRAVITY OF LAMPBLACK.

By William Hallock.

The six samples of lampblack which formed the subject of this investigation were kindly furnished by Mr. Samuel Cabot, manufacturer of lampblack, in Boston, as samples of the different grades of commercial lampblack made by him. With the six samples came the following specifications with regard to the source or method of the manufacture of each:

I. Black from kerosene.
II. Black from coal tar naphtha.
III. Black from natural gas.
IV. Black from dead oil.[1]
V. Black from dead oil; very hot.[2]
VI. Black from dead oil; very light and fine.[3]

In order to get more nearly the pure lampblack, free from oil, &c., in each case, all the samples were washed in benzol, alcohol, and boiling water and dried at 180° C.

The following table will show the effects of the above washings; also, the percentage of ash, the original weight of the substance after standing fifteen hours in a desiccator being 100 per cent.

Number of sample.	I.	II.	III.	IV.	V.	VI.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Dried at 180° C	98.5	99.0				
Washed with alcohol and dried at 180° C	97.0	98.0	99.4	96.9	98.2	98.5
Washed with water at 100° and dried at 180° C	96.9	....	....	....	....	....
Washed with benzol and dried at 180° C.	96.9	....	....	....	....	....
Ignited in O. ash	0.08	0.3	0.45	0.08	0.2	0.02

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[1] This sample is from the back part of the receiving house, where small furnaces are used, and therefore the black is not highly heated.

[2] This sample is from houses where the furnaces are very large; therefore the black is exposed to a high degree of heat. It gives a large yield and is a cheap black.

[3] This sample is fine black from near the furnaces in the same receivers as IV.

The portions used for the determinations were washed in benzol, alcohol, and boiling water, dried at 180° C., and weighed after being in the balance case long enough to have a constant weight; of this point the particulars will be given later.

The specific gravity was determined by the pycnometer, using 10 per cent. alcohol as the liquid. The specific gravity of this was found to be 0.9864 at 20°.0C. In each case the sample was weighed dry in the pycnometer, then covered with 10 per cent. alcohol and put under the receiver of an air pump for several hours, until air was no longer given off. A test determination demonstrated that this did not appreciably alter the specific gravity of the liquid. After that the vessel was carefully filled, so as not to stir up the carbon settled on the bottom, the stopper put in, and the whole was weighed; then the stopper was removed and a small delicate thermometer was inserted into the liquid and the temperature noted. The pycnometer was then again closed, weighed, &c. Thus there were obtained three readings of the temperature and three weighings, the mean of which in each case served to calculate the specific gravity.

In this way the following values were found:

No. I.	1.7231 1.7233 1.7227	1.723	No. IV.	1.7668 1.7665 1.7670	1.767
No. II.	1.7797 1.7797 1.7803	1.780	No. V.	1.7890 1.7887 1.7881	1.789
No. III.	1.7513 1.7521 1.7521	1.752	No. VI.	1.7637 1.7636 1.7641	1.764

Too much reliance must not be placed upon these values, owing to the fact that the lampblack condenses on its surface a large amount of air, which is weighed with it when the weighing in air is made, but is absent when it is covered with the liquid. An idea of the extent to which this may affect the determinations may be obtained from the following statement.

A sample of No. II was taken after the washings and dryings, similar to that used for the specific gravity. The original weight is called 100 per cent.

Heated 2^h to 180°, then 24^h in H_2SO_4 desiccator	*a*	98.8
Heated 1^h to 180°, then 2^h in H_2SO_4 desiccator	*b*	98.7
5^h in balance case	*c*	100.55
Heated 3^h to 180°, then 40^m in H_2SO_4 desiccator	*d*	98.76
2 months in H_2SO_4 desiccator	*e*	99.2

Thus it appears probable the *dry carbon, free from air*, weighs only 98.75 per cent. (mean of *a*, *b*, *d*) of the weight as it comes from the sample tube and as used above for the specific gravity. This, if it is general, would lower the above values of the specific gravity by about 1.25 per cent., or 0.022.

An attempt was also made to obtain some idea of the size of the grains of the black by the rate of sedimentation, on the principle that the finer the particles the slower the sedimentation. For example, a *single* particle falls through a liquid with a velocity proportional to the square of its diameter (radius).

For this purpose 0.1 gr. of each sample was taken from that used for the determination of the specific gravity and placed in test tubes about 20^{mm} by 120^{mm} dimensions. Upon each was poured 3^{cc} of alcohol, then ten shot, 2^{mm} in diameter, were put in each tube to help break up the black. After vigorous shaking 5^{cc} of water was added; then the tubes were heated till the liquid boiled, placed under the receiver of an air pump, and the pressure was reduced till they boiled there, when they were left 18^{h} to remove any air which might be condensed on the surface of the carbon. The tubes were then filled with distilled water well shaken and stood up to sedimentate.

After standing for the time given in the ninth column, Table I, two-thirds of the liquid was poured into another tube and that placed aside. The original tube was then refilled with distilled water, well shaken, and stood up until the next decantation, and so on, until the contents of the original tube would settle in a day or less. Thus each sample was separated into a series of lots of different fineness. The time required by these decanted lots to settle is given in Table II.

Unfortunately these results cannot be expressed in a very clear way, but in general the following is true:

Sample I. Settles quite completely in fifteen minutes, and hence is coarse.

Sample II. Settles in one day, and is hence much finer than I and III, but not so fine as IV, V, or VI.

Sample III. Same as sample I.

Sample IV. A little finer and slower than No. II.

Sample V and VI. These two are very nearly alike and are both *much* finer than any of the rest. Sample VI is, however, decidedly the finer of the two.

Of course any sample may behave as if it were coarse when each grain is, in fact, an agglomeration of several. This is hardly likely in the the above samples, since, if such were the case, we would be apt to find some fine black even in samples I and III.

I am fully aware of the incomplete and primitive character of this investigation, and sincerely hope it may incite some one with plenty of time and energy to take up the subject thoroughly and either confirm or refute my conclusions.

TABLE I.

Number of decantation.	Time of decantation.	Sample I.	Sample II.	Sample III.	Sample IV.
1	May 28, 1886, 11.45 a. m.	Clear after 15 m.	Opaque	Clear after 15 m.	Opaque.
2	12.2 p. m.	Discontinued	....do	Discontinued	Do.
3	2		Translucent		Do.
4	3. 25		....do		Dimly translucent.
5	3. 55		....do		Do.
6	May 29, 1886, 11 a. m.		Very translucent.		Medium translucent.
7	12. 30 p. m		Discontinued		Medium translucent; settles now in a few hours.

Number of decantation.	Time of decantation.	Sample V.	Sample VI.	Interval between decantations or shaking.	Total time since commenced.
1	May 28, 1886, 11.45 a. m.	Opaque	Opaque	1 h. 55 m	1 h. 55 m.
2	12. 2 p. m	....do	....do	17 m	2 h. 12 m.
3	2	....do	....do	1 h. 58 m	4 h. 10 m.
4	3. 25	....do	....do	1 h. 25 m	5 h. 35 m.
5	3. 55	....do	....do	30 m	6 h. 5 m.
6	May 29, 1886, 11 a. m.	Very weakly translucent.	....do	1 h. 30 m	7 h. 35 m.
7	12. 30 p. m	Very weakly translucent; settles now in a few hours.	Opaque; settles now in a day or so.	1 h. 30 m	9 h. 5 m.

TABLE II.

Decantation.	Sample I.	Sample II.	Sample III.	Sample IV.	Sample V.	Sample VI.
1	Less than 1 hour.	Less than 1 hour.	Less than 1 hour.	Less than 5 days.	Not in 20 days.	Not in 30 days.
2		....do		....do	Translucent in 5 days.	Do.
3		....do		....do	....do	Translucent in 20 days.
4				1 day	Clear in 5 days.	Translucent in 5 days.
5				Less than 1 hour.	Clear in 1 day.	Do.
6				....do	....do	Do.
7				....do	....do	Translucent in 1 day.

MISCELLANEOUS ANALYSES.

THE PERIDOTITE OF ELLIOTT COUNTY, KENTUCKY.[1]

[Specimens collected by J. S. Diller and analyzed by T. M. Chatard.]

A. Peridotite.
B. Olivine from peridotite.
C. Pyrope from peridotite.
D. Ilmenite from peridotite.
E. Syenite inclusion.
F. Slaty inclusion.
G. Calcareous sandstone near peridotite dike.
H. Indurated shale near peridotite dike.
I. Fine grained, fissile sandstone near dike.

	A.	B.	C.	D.
H_2O at 110°	8.92	.14	.17	.20
H_2O at red heat	......	.66		
CO_2	6.66	......	......	......
SiO_2	29.81	40.05	41.32	.76
TiO_2	2.20	.07	.16	49.32
P_2O_5	.35	.04	None	Trace
Cr_2O_3	.43	.24	.91	.74
Al_2O_3	2.01	.39	21.21	2.84
Fe_2O_3	5.16	2.36	4.21	9.13
FeO	4.35	7.14	7.93	27.81
MnO	.23	.20	.34	.20
CoO	......	Trace	......	......
NiO	.05	......	......	......
CaO	7.69	1.16	4.94	.23
MgO	32.41	46.68	19.32	8.68
K_2O	.20	.21	.07	.19
Na_2O	.11	.08		
SO_3	.28	......	......	......
	100.86	99.42	100.58	100.10

---

[1] Discussed by J. S. Diller in Am. Jour. Sci., August, 1886.

	E.	F.	G.	H.	I.
H_2O at 110°	.51	1.40	.85	......	1.94
H_2O at red heat		9.00	2.32	8.78	5.17
CO_2	......	.88	6.29	.55	......
SiO_2	60.56	35.53	60.78	41.32	60.25
TiO_2	1.19	.95	.03	.48	.23
P_2O_5	.30	.08	.09	.08	.10
Cr_2O_3	......	......	......	Trace	......
Al_2O_3	16.19	18.23	10.54	20.71	20.18
Fe_2O_3	5.19	2.46	3.27	2.59	1.53
FeO	2.41	4.81	......	5.46	3.42
MnO	.36	.13	.10	.17	.10
CaO	2.09	21.17	10.15	9.91	.51
MgO	1.30	2.01	1.59	1.91	3.52
K_2O	4.82	1.08	2.36	.88	3.17
Na_2O	4.78	2.53	1.41	7.19	.39
	99.70	100.26	99.78	100.03	100.51

TRENTON LIMESTONE FROM LEXINGTON, VA.

[Collected by H. D. Campbell. Analyses by R. B. Riggs.]

A. Limestone.
B. Residual deposit from subaërial decay of limestone.

	A.	B.
Ignition	1.08	12.98
CO_2	42.72	......
SiO_2	.44	43.07
Al_2O_3	......	25.07
Fe_2O_3	.42	15.16
CaO	54.77	.63
MgO	Trace	.03
K_2O	......	2.50
Na_2O	......	1.20
	99.43	100.64

RESIDUAL DEPOSIT FROM SUBAËRIAL DECAY OF CHLORITIC SCHIST FROM EIGHT MILES WEST OF CARY, N. C.

[Collected by I. C. Russell. Analysis by R. B. Riggs.]

SiO_2	54.54
Al_2O_3	26.43
Fe_2O_3	9.04
Ignition	9.87
	99.88

YELLOWISH BROWN, KAOLINIZED, DECOMPOSED TRAP FROM FOUR MILES WEST OF SANFORD, N. C.

[Collected by I. C. Russell. Analysis by T. M. Chatard.]

Ignition	13.26
SiO_2	39.55
Al_2O_3	28.76
TiO_2	.64
P_2O_5	.10
Fe_2O_3	16.80
Cr_2O_3	Trace
MnO	Trace
CaO	.37
MgO	.59
Alkali	Undet.
	100.07

ALTERED FELDSPAR FROM LAUREL CREEK, GA.

[Analysis by T. M. Chatard.]

H_2O	8.68
SiO_2	49.25
Al_2O_3	36.33
Fe_2O_3	.09
MnO	None
CaO	3.17
MgO	.64
K_2O	.26
Na_2O	2.16
	100.58

FERRUGINOUS ROCK FROM PENOKEE IRON RANGE,[1] WISCONSIN.

[Collected by R. D. Irving. Analysis by R. B. Riggs.]

SiO_2	15.62
Al_2O_3	4.27
Fe_2O_3	8.14
FeO	32.85
MnO	5.06
CaO	.81
MgO	2.66
CO_2	30.32
H_2O	.68
	100.41

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[1] From NE. ¼ of Sec. 6, T. 45, R. 2 E.

TWO ROCKS FROM KAKABIKKA FALLS, KAMINISTIQUIA RIVER, ONTARIO, CANADA.

[Collected by R. D. Irving. Analyses by R. B. Riggs.]

A. Black slate, Animikie formation.

B. Material interstratified with the foregoing.

	A.	B.
SiO_2	37.73	54.26
Al_2O_3	3.41	2.57
Fe_2O_3	6.42	3.62
FeO	22.92	19.63
MnO	.40	.19
CaO	1.26	1.07
MgO	3.98	2.93
CO_2	18.01	14.93
H_2O	2.74	1.20
C	3.54	.45
	100.41	100.85

MICA ANDESITE FROM A CAÑON ON THE EAST SIDE OF SAN MATEO MOUNTAIN, NEW MEXICO.

[Collected by Capt. C. E. Dutton. Analysis by T. M. Chatard.]

Ignition	.14
SiO_2	65.78
TiO_2	.27
P_2O_5	.13
Al_2O_3	17.32
Fe_3O_3	3.68
FeO	.46
MnO	.32
CaO	1.66
MgO	.47
K_2O	4.64
Na_2O	5.23
	100.10

HYPERSTHENE ANDESITE FROM SAN FRANCISCO MOUNTAINS, ARIZONA.

[Collected by Capt. C. E. Dutton. Analysis by T. M. Chatard.]

Ignition	.20
SiO_2	64.82
TiO_2	.56
P_2O_5	.23
Al_2O_3	18.27
Fe_2O_3	3.48
FeO	.56
MnO	.20
CaO	2.89
MgO	.85
Na_2O	5.05
K_2O	2.67
	99.78

BASALT FROM SIX MILES NORTHEAST OF GRANT, NEW MEXICO.

[Collected by Capt. C. E. Dutton. Analyses by T. M. Chatard. Separations of minerals by J. S. Diller.]

A. Basalt.
B. Separated augite.
C. Separated feldspar.

	A.	B.	C.
H_2O	.36	.20	.26
SiO_2	47.54	47.06	52.54
TiO_2	2.76	1.82	Undet.
P_2O_5	.51	.06	....
Al_2O_3	16.73	7.77	31.26[1]
Fe_2O_3	6.69	1.30	
FeO	6.67	8.15	....
MnO	.19	.20	....
BaO	.03	......	Trace
CaO	8.74	19.33	12.34
MgO	6.38	13.52	.28
Na_2O	2.81	.33	3.55
K_2O	1.10	.11	.42
	100.51	99.85	100.65

In B there were traces of Cr, Co, and Ni. Analysis C was made from only .75 gramme of material.

FULGURITE FROM WHITESIDE COUNTY, ILLINOIS.

[Analyses by F. W. Clarke of material selected by G. P. Merrill.]

	Fused glassy portion.	Adjacent sand.
Ignition	.33	1.01
SiO_2	91.66	84.83
Al_2O_3 Fe_2O_3	6.69	9.88
CaO	.38	1.16
MgO	.12	.13
K_2O	.73	1.13
Na_2O	.77	1.50
	100.68	99.64

The fact of the excess of silica in the fulgurite proper was verified by duplicate determinations.

BLUE AND BUFF LIMESTONES FROM QUARRIES OF THE HOOSIER STONE COMPANY, BEDFORD, INDIANA.

[Analyses by F. W. Clarke.]

	Blue.	Buff.
CO_2	43.08	44.01
SiO_2	1.69	.63
Fe_2O_3	.49	.39
CaO	54.18	54.19
MgO	.37	.39
P_2O_5	Trace	Trace
	99.81	99.61

---

[1] Little Fe_2O_3.

Alkalies undetermined. The color of the buff stone is due largely to organic or carbonaceous matter.

YELLOW SANDSTONE[1] FROM THE ARMEJO QUARRY, COLORADO.

[Analyses by T. M. Chatard.]

A. Analysis (partial) by treatment with strong hydrochloric acid.
B. Analysis by fusion with carbonate of soda.

	A.		B.
Insoluble in HCl	95.54	H_2O	1.19
Soluble:		SiO_2	81.27
Fe_2O_3 Al_2O_3	2.36	Al_2O_3	9.81
CaO	.17	Fe_2O_3	1.44
MgO	.34	CaO	.44
H_2O	1.19	MgO	.42
		Undet	5.43
	99.60		100.00

The undetermined portion under B was probably all alkalies.

EIGHT SAMPLES OF VOLCANIC DUST.

[Series A. From Gallatin Valley, Mont. Collected by A. C. Peale. Analyses by F. W. Clarke.]

[1. Dry Creek Valley, above mouth of Pass Creek. 2 and 3. From near Bozeman. 4. From near Fort Ellis.]

	1.	2.	3.	4.
H_2O	6.45	11.47	6.34	11.96
SiO_2	46.09	61.82	71.01	60.98
Al_2O_3, Fe_2O_3	14.35	19.86	15.17	21.69
CaO	1.61	1.78	1.19	1.83
$CaCO_3$	28.72	....	....	....
MgO	1.29	.51	.34	1.33
K_2O	1.47	1.31	2.97	1.23
Na_2O		2.38	2.77	.80
	99.98	99.13	99.79	99.82

[Series B. Material furnished by G. P. Merrill. Analyses by J. Edward Whitfield.]

[1. From Marsh Creek Valley, Idaho. 2. From Little Sage Creek, Montana. 3. From Devil's Pathway, Montana.]

	1.	2.	3.
H_2O lost at 105°	1.60	1.12	3.46
Ignition	6.00	6.50	5.60
SiO_2	68.92	65.56	65.76
Al_2O_3, Fe_2O_3	16.22	18.24	17.18
CaO	1.62	2.58	2.30
MgO	Trace	.72	Trace
K_2O	4.00	3.94	3.14
Na_2O	1.56	2.08	2.22
	99.92	100.74	99.66

---

[1] In use as a building stone.

[Series C. From mouth of Bazile Creek, Nebraska. Collected by J. E. Todd. Partial analysis by F. W. Clarke.]

Ignition	4.58
SiO_2	73.67
Al_2O_3 Fe_2O_3	14.33
CaO	.87
MgO	Trace
Alkalies	Undet.

LOESS AND CLAYS.

[Collected by Prof. T. C. Chamberlin. Analyses by R. B. Riggs. Material dried at 100°.]

[A. Typical loess, Kansas City, Mo.]

SiO_2	74.46
Al_2O_3	12.26
P_2O_5	.09
TiO_2	.14
Fe_2O_3	3.25
FeO	.12
MnO	.02
CaO	1.69
MgO	1.12
K_2O	1.83
Na_2O	1.43
H_2O (includes H of organic matter)	2.70
CO_2	.49
C. (organic)	.12
SO_3	.06
Cl	.05
	99.83

[B. Loess from 300 feet above the Mississippi River, 3½ miles northwest of Dubuque, Iowa.]

SiO_2	72.68
Al_2O_3	12.03
TiO_2	.23
P_2O_5	.72
Fe_2O_3	3.53
FeO	.96
MnO	.06
CaO	1.59
MgO	1.11
K_2O	2.13
Na_2O	1.68
H_2O (includes H of organic matter)	2.50
CO_2	.39
C (organic)	.09
SO_3	.51
Cl	.01
	100.22

[C. Loess from seven foot stratum over brown residuary clay, 350 feet above Mississippi River, near Galena, Ill.]

SiO_2	64.61
Al_2O_3	10.64
P_2O_5	.06
TiO_2	.40
Fe_2O_3	2.61
FeO	.51
MnO	.05
CaO	5.41
MgO	3.69
K_2O	2.06
Na_2O	1.35
H_2O (includes H of organic matter)	2.05
CO_2	6.31
C (organic)	.13
SO_3	.11
Cl	.07
	100.06

[D. Loess from center of the city, Vicksburg, Miss.]

SiO_2	60.69
Al_2O_3	7.95
P_2O_5	.13
TiO_2	.52
Fe_2O_3	2.61
FeO	.67
MnO	.12
CaO	8.96
MgO	4.56
K_2O	1.08
Na_2O	1.17
H_2O (includes H of organic matter)	1.14
CO_2	9.63
C (organic)	.19
SO_3	.12
Cl	.08
	99.62

[E. Red, putty-like clay with pebbles, Milwaukee, Wis.]

SiO_2	40.22
Al_2O_3	8.47
P_2O_5	.05
TiO_2	.35
Fe_2O_3	2.83
FeO	.48
MnO	Trace
CaO	15.65
MgO	7.80
K_2O	2.36
Na_2O	.84
H_2O (includes H of organic matter)	1.95
CO_2	18.76
C (organic)	.32
SO_3	.13
Cl	.06
	100.27

[F. Red pebble clay, from 15 feet below Lower Beach deposit, Milwaukee, Wis.]

SiO_2	48.81
Al_2O_3	7.54
P_2O_5	.13
TiO_2	.45
Fe_2O_3	2.53
FeO	.65
MnO	.03
CaO	11.83
MgO	7.05
K_2O	2.60
Na_2O	.92
H_2O (includes H of organic matter)	2.02
CO_2	15.47
C (organic)	.38
SO_3	.05
Cl	.04
	100.50

IRON ORES FROM LOUISIANA.

[Analyses by R. B. Riggs.]

[A. Brown hematite from Bossier Parish, one-half mile west of Bellevue.]

Ignition	11.06
SiO_2	27.85
Fe	39.65
S	.03
Mn	.126
P	.226

[B. Brown hematite from Dr. Whitlaw's, four miles west of Greenwood, Caddo Parish.]

Ignition	10.26
SiO_2	6.37
Fe	50.32
S	.10
Mn	.079
P	Trace

[C. Brown hematite from Simmons's bed, eight miles south of Homer, Claiborne Parish.]

Ignition	10.53
SiO_2	21.77
Fe	43.17
S	.26
Mn	.01
P	.382

[D. Brown hematite from Moreland's, nine miles southeast of Homer, Claiborne Parish.]

Ignition	10.62
SiO_2	10.97
Fe	52.18
S	.03
Mn	.026
P	.064

[E. Brown hematite from 500 feet east of Vienna wire road, Lincoln Parish.]

Ignition	9.05
SiO_2	23.20
Fe	44.54
S	.09
Mn	.006
P	.859

[F. Brown hematite from Lincoln Reed's place, nine miles northwest of Vienna.]

Ignition	9.50
SiO_2	28.12
Fe	39.26
S	.03
Mn	.049
P	.447

[G. Brown hematite from Webster, four miles northwest of Shangaloo.]

Ignition	11.25
SiO_2	18.72
Fe	45.72
S	.17
Mn	.007
P	.247

[H. Brown hematite from Union Parish, one and a half miles north of Downsville.]

Ignition	11.04
SiO_2	21.70
Fe	43.76
S	.03
Mn	.005
P	.835

[I. Brown hematite from Moreland's, ten miles southwest of Arcadia, Bienville Parish.]

Ignition	18.22
SiO_2	39.95
Fe	22.22
S	.17
Mn	.157
P	.072

[J. Limestone from Rayborn's Salt Lick, Bienville Parish.]

SiO_2	.55
$Fe_2O_3Al_2O_3$	1.61
P_2O_5	.048
MnO	Trace
CaO	54.09
MgO	.06
CO_2	44.12
SO_3	.05
	100.528

"NATURAL COKE" FROM MIDLOTHIAN, VA.

[Collected by I. C. Russell. Analysis by R. B. Riggs.]

Water	1.66
Volatile matter	18.35
Fixed carbon	67.13
Ash	12.86
	100.00
Sulphur	4.70

Water in coal dried forty-eight hours over sulphuric acid, 0.11 per cent. Water taken up in forty-eight hours' exposure over water, 3.90 per cent.

COAL FROM JEFFERSON COUNTY, WEST VIRGINIA.

[Bed about fifteen miles west of Berkeley Springs. Analysis by J. Edward Whitfield.]

Moisture	2.30
Volatile matter	10.90
Fixed carbon	81.20
Ash	5.60
	100.00
Sulphur	.785

No coke; ash, pink and sandy.

THREE COALS FROM GULF, NORTH CAROLINA.

[Collected by I. C. Russell. Analyses by F. W. Clarke. Specific gravity determinations made with the Jolly balance by E. L. Howard.]

	Upper layer.	Middle layer.	Lower layer.
Volatile matter	24.48	24.22	23.94
Fixed carbon	72.44	67.86	66.37
Ash	3.08	7.92	9.69
	100.00	100.00	100.00
Sulphur	.99	1.42	3.33
Specific gravity	1.295	1.339	1.359

Coke, good; ash, gray. The coals gain weight on drying at 115°.

COAL FROM WALNUT COVE, STOKES COUNTY, NORTH CAROLINA.

[Analysis by J. Edward Whitfield.]

Water	.38
Volatile matter	17.99
Fixed carbon	55.47
Ash	26.16
	100.00
Sulphur	5.56

No coke. Residue sandy.

"NATURAL COKE" FROM PURGATORY CAÑON, NEW MEXICO.

[Analysis by R. B. Riggs.]

Volatile matter	16.87
Fixed carbon	74.18
Ash	8.95
	100.00
Specific gravity	1.43

TWO SPRINGS, ONE MILE FROM FARMWELL STATION, LOUDOUN COUNTY, VIRGINIA.

[Analyses by R. B. Riggs. Stated in grammes per liter.]

A.

	Found.	Per cent. of total solids.	Hypothetical combination.	
SO_4	1.2865	61.10	KCl	.0067
Cl	.0095	.45	$NaCl$	.0104
CO_3	.1590	7.55	Na_2SO_4	.2355
SiO_2	.0210	1.00	$MgSO_4$	.0750
Al_2O_3	.0070	.33	$CaSO_4$	1.5052
Ca	.5235	24.87	$CaH_2(CO_3)_2$	.1100
Mg	.0150	.71	$CaCO_3$	.1319
K	.0035	.17	Al_2O_3	.0070
Na	.0805	3.82	SiO_2	.0210
	2.1055	100.00		2.1027

B.

SO_4	1.4050	61.28	KCl	.0057
Cl	.0175	.76	$NaCl$	.0244
CO_3	.1730	7.55	Na_2SO_4	.2543
SiO_2	.0110	.48	$MgSO_4$	.0975
Al_2O_3	.0105	.46	$CaSO_4$	1.6363
Ca	.5610	24.47	$CaH_2(CO_3)_2$	.1438
Mg	.0195	.85	$CaCO_3$	.1107
K	.0030	.13	Al_2O_3	.0105
Na	.0920	4.01	SiO_2	.0110
	2.2925	99.99		2.2942

TWO ARTESIAN WELLS, STORY CITY, STORY COUNTY, IOWA.

[Analyses by F. W. Clarke, with carbonic acid determinations by R. B. Riggs.]

[A. Water from artesian well of Thorkill Henryson. Total solids, 0.3620 gramme to liter.]

	Found.	Per cent. of total solids.	Hypothetical combination.	
SiO_2	Trace		SiO_2	Trace
Fe_2O_3 $Al_2.O_3$	.0135	3.73	Fe_2O_3, Al_2O_3	.0135
Cl	.0010	.27	NaCl	.0016
SO_4	None		Na_2CO_3	.0417
Ca	.0764	21.10	$CaCO_3$	.1910
Mg	.0324	8.95	$MgCO_3$	.1134
Na	.0187	5.17		
CO_2, total	.2680	CO_3 60.56		.3612
		99.78	(99.78 per cent. of total solids accounted for.)	

The CO_2 required in the second and third columns is 0.1607 gramme, leaving 0.1083 gramme for bicarbonates. The water contained flakes of ferric hydroxide.

[B. Water from artesian well of Charles Watkins. Total solids, 0.4710 gramme to liter.]

	Found.	Per cent. of total solids.	Hypothetical combination.	
SiO_2	.0250	5.31	SiO_2	.0250
Fe_2O_3	.0060	1.28	Fe_2O_3	.0060
Ca	.0796	16.90	$CaCO_3$	.1990
Mg	.0356	7.56	$MgCO_3$	.1246
Na	.0501	10.64	Na_2CO_3	.1155
K	Trace	CO_3 58.12		
				.4701
Cl	Trace	99.81	(99.81 per cent. of total solids accounted for.)	
CO_2, total	.3920			

The CO_2 required in the second and third columns is .2008 gramme, leaving .1912 gramme for bicarbonates. The water contained much sediment. Neither water contained any sulphates.

BECK'S HOT SPRINGS, NEAR SALT LAKE CITY, UTAH.

[Analysis by R. B. Riggs. Stated in grammes per liter.]

	Found.	Per cent. of total solids.	Hypothetical combination.	
SO_4	.8405	6.68	KCl	.3761
Cl	6.7438	53.59	NaCl	9.5506
CO_3	.2045	1.63	$MgCl_2$	.4334
SiO_2	.0315	.25	$CaCl_2$	.6957
Al_2O_3	.0090	.07	$CaSO_4$	1.1907
Ca	.6943	5.52	$CaCO_3$	.1262
Mg	.1095	.85	$CaH_2(CO_3)_2$	.1739
K	.1969	1.57	Al_2O_3	.0090
Na	3.7549	29.84	SiO_2	.0315
Li	Trace			
B_2O_3	Trace			12.5871
	12.5849	100.00		

WATER OF MONO LAKE, CALIFORNIA.

[Analysis by T. M. Chatard. Compare old analysis in Bulletin 9, p. 26. Stated in grammes per liter. Specific gravity, 1.0456, 17.°5.]

	Found.	Per cent. of total solids.
Na	19.6853	36.790
K	.9614	1.795
Ca	.0200	.037
Mg	.0551	.103
Al_2O_3, Fe_2O_3	.0030	.005
SiO_2	.0700	.130
SO_4	6.6720	12.470
Cl	12.1036	22.630
B_4O_7	.1600	.300
CO_2	10.0396	18.770
O for CO_3	3.2341	6.090
H_2O in bicarbonates	.4683	.880
	53.4724	100.000

Hypothetical combination.	
KCl	1.8342
NaCl	18.5068
Na_2SO_4	9.8690
Na_2CO_3	18.6720
$NaHCO_3$	3.9015
$Na_2B_4O_7$	.2000
$CaH_2(CO_3)_2$	.0810
$MgH_2(CO_3)_2$	.3349
Al_2O_3,Fe_2O_3	.0030
SiO_2	.0700
	53.4724

The boric acid is cited from the old analysis, as the material was insufficient for a new determiation.

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