ON THE ACTION OF HYDROFLUORIC ACID ON SILICA AND SILICATES.

By J. B. MACKINTOSH.

In a preliminary note on this subject, published in July, 1886,* I called attention to the great difference in the behavior of quartz and opal, when submitted to the action of hydrofluoric acid, and gave a general indication of the behavior of silicates under similar circumstances. The few data contained in the above mentioned note will be all included in the present paper, which I hope may be regarded as an acceptable contribution to the literature of the silicates.

The starting point of the present investigation arose from a question which occasionally presented itself in the course of my professional work. I have frequently been appealed to to decide upon the identity of cut and polished gems, without, of course, subjecting them to injury in any way. Chemical analysis being out of the question, it is necessary to make the determination by means of the physical characteristics alone, but in certain cases it becomes a very difficult matter to decide. The two gems, garnet and spinel, occurring in varying shades of color, although generally readily distinguished, yet occasionally approach so closely in their characteristics that I attempted to find a means of differentiation based on their chemical constitution, which, while it would have the certainty of a qualitative analysis, would leave the gem practically uninjured. Spinel being a compound of protoxide with a sesquioxide in equal molecular proportions, while garnet is a silicate which may be regarded as derived from spinel by the substitution of an equivalent amount of silica for two-thirds of the sesquioxide present, it seemed probable that hydrofluoric acid would furnish the means of differentiation sought for, but on making the experiment it was found that neither mineral was attacked in the slightest degree. This unexpected result was so interesting that I determined to extend the investigation further than I had originally purposed and to examine in this way the principal silicates occurring in nature.

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* School of Mines Quarterly, No. 4, Vol. 7.

The following tables show the results of the qualitative experiments I have made. I have included in these tables the atomic formulæ, the specific gravity, the unit volume and the percentage of silica in the mineral. For the first three data I am indebted to Dr. T. Sterry Hunt and have taken most of them from his recently published essay on "A Natural System of Mineralogy, with a classification of Native Silicates."*

The atomic formulæ are those employed by Sterry Hunt and differ from ordinary formulæ, in that the quantities represented by the symbols of the elements are all equivalent to one atom of hydrogen. The coefficients thus represent the oxygen ratios of the constituents, and the formulæ are very much simplified.

I.—MINERALS WHICH ARE VISIBLY ETCHED BY HYDROFLUORIC ACID.

	ATOMIC FORMULA.	Sp. Gr.	Volume	% SiO_2.	REMARKS.
Quartz	$si_1\ o_1$	2.67	5.62	100.	very slightly attacked.
Opal	$si_1\ o_1$	2.2	6.81	100. ?	H_2O regarded as non-essential.
Petalite	$(li_1\ al_4\ si_{20})\ o_{25}$	2.42	6.33	78.	
Wollastonite	$(ca_1\ si_2)\ o_3$	2.92	6.62	51.7	
Rhodonite	$(mn_1\ si_2)\ o_3$	3.63	6.06	46.7	
Tremolite	$((mg_{3/4}\ ca_{1/4})\ si_2)\ o_3$	2.97	5.88	57.4	very slightly attacked.
Willemite	$(zn_1\ si_1)\ o_2$	4.18	6.63	27.5	
Chrysolite	$(mg_1\ si_1)\ o_2$	3.40	5.38	45.	
Fayalite	$(fe_1\ si_1)\ o_2$	4.35	5.86	27.3	very slightly attacked.
Wernerite	$(m_4\ al_9\ si_{16})\ o_{29}$	2.70	6.44	48.5	
Vesuvianite	$(ca_3\ al_2\ si_5)\ o_{10}$	3.40	5.67	37.	very slightly attacked.
Biotite	$(mg_4\ al_4\ si_8)\ o_{16}$	3.00	6.06	41.	very slightly attacked.
Phlogopite	$(mg_4\ al_2\ si_6)\ o_{12}$	2.85	6.35	40.	very slightly attacked.
Iolite	$((mg_{2/3}\ fe_{1/3})\ al_3\ si_5)\ o_9$	2.67	6.31	49.	
Albite	$(na_1\ al_3\ si_{12})\ o_{16}$	2.62	6.24	68.6	
Orthoclase	$(k_1\ al_3\ si_{12})\ o_{16}$	2.54	6.83	64.6	
Oligoclase	$((na_{3/4}\ ca_{1/4})\ al_3\ si_9)\ o_{13}$	2.65	6.27	61.5	
Labradorite	$((ca_{3/4}\ na_{1/4})\ al_3\ si_6)\ o_{10}$	2.70	6.28	55.5	
Leucite	$(k_1\ al_3\ si_8)\ o_{12}$	2.56	7.09	55.	
Titanite	$(ca_1\ si_2\ tl_2)\ o_5$	3.50	5.65	30.5	
Datolite	$(ca_2\ si_4\ b_3\ h_1)\ o_{10}$	2.99	5.35	37.5	very slightly attacked.
Apophyllite	$(ca_1\ si_4)\ o_5 + 2\ aq$	2.35	6.44	53.	
Pectolite	$(ca_5\ si_{12})\ o_{17} + 1\ aq$	2.78	6.57	54.6	
Calamine	$(zn_1\ si_1)\ o_2 + \frac{1}{2}\ aq$	3.50	6.87	25.	
Prehnite	$(ca_2\ al_3\ si_6)\ o_{11} + 1\ aq$	2.95	5.64	43.6	etched with difficulty.
Heulandite	$(ca_1\ al_3\ si_{12})\ o_{16} + 5\ aq$	2.20	6.58	59.	
Stilbite	$(ca_1\ al_3\ si_{12})\ o_{16} + 6\ aq$	2.20	6.46	57.4	
Harmatome	$(ba_1\ al_3\ si_{10})\ o_{16} + 5\ aq$	2.45	6.82	46.5	
Chabazite	$(ca_1\ al_3\ si_8)\ o_{12} + 6\ aq$	2.19	6.41	52.2	
Analcite	$(na_1\ al_3\ si_8)\ o_{12} + 2\ aq$	2.29	6.86	54.5	
Natrolite	$(na_1\ al_3\ si_6)\ o_{10} + 2\ aq$	2.25	7.03	47.3	
Serpentine	$(mg_3\ si_4)\ o_7 + 2\ aq$	2.53	5.78	42.	
Halloysite	$(al_3\ si_4)\ o_7 + 3\ aq$	2.40	5.75	43.3	
Jeffriesite	$(mg_6\ al_6\ fl_3\ si_{15})\ o_{30} + 7\frac{1}{2}\ aq$	2.30	6.50	34.	

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*This essay forms pp. 279-401 of his Mineral Physiology and Physiography. 1886, S. E. Cassino, Boston, Mass.

II.—MINERALS WHICH ARE NOT VISIBLY ETCHED BY HYDROFLUORIC ACID.

	ATOMIC FORMULA.	Sp. Gr.	Volume	% SiO_2.	REMARKS.
Quartz.	$si_1\ o_1$	2.67	5.62	100.	some varieties.
Enstatite	$(mg_1\ si_2)\ o_3$	3.10	5.54	60.	
Diopside	$((mg\ ca)_1 si_2)\ o_3$	3.28	5.48	54.	
Spodumene	$(li_1\ al_4\ si_{10})\ o_{15}$	3.18	4.88	64.	
Beryl	$(be_3\ al_3\ si_{12})\ o_{18}$	2.70	5.52	67.	
Tremolite	$(mg\frac{3}{4}\ ca\frac{1}{4}\ si_2)\ o_3$	2.97	5.88	57.4	slightly attacked by long exposure.
Zircon	$(zr_1\ si_1)\ o_2$	4.70	4.84	33.	
Garnet	$(ca_1\ al_1\ si_2)\ o_4$	3.50	5.37	36.	
Epidote	$(ca_1\ al^4/_3\ fe\frac{2}{3}\ si_3)\ o_6 + \frac{1}{3}\,aq.$	3.40	5.40	38.	
Zoisite	$(ca_1\ al_2\ si_3)\ o_6$	3.35	5.32	44.	
Axinite	$(ca_1\ al^4/_3\ fe\frac{2}{3}\ b\frac{1}{2}\ si_3\frac{1}{2})\ o_7$	3.27	5.53	44.	
Danburite	$(ca_1\ b_3\ si_4)\ o_8$	3.00	5.12	48.	
Lepidolite	$(m_1\ al_4\frac{1}{2}\ si_8)\ o_{13}\frac{1}{2}$	3.00	5 61	46.5	
Muscovite	$(k_1\ al_6\ si_9)\ o_{16}$	3.12	5.68	46.5	
Biotite	$(m_4\ (al\ fe)_4\ si_8)\ o_{16}$	3.00	6.06	41.	very slightly attacked.
Phlogopite	$(m_4\ al_2\ si_6)\ o_{12}$	2.85	6.35	40.	very slightly attacked.
Fayalite	$(fe_1\ si_1)\ o_2$	4.35	5.86	27.3	very slightly attacked.
Tourmaline	$(m_1\ al_3\ si_5)\ o_9$	3.05	5.36	37.5	
Andalusite	$(al_3\ si_2)\ o_5$	3.35	4.83	37.5	
Cyanite	$(al_3\ si_2)\ o_5$	3.66	4.42	37.5	
Topaz	$(al_3\ si_2)\ o_4\ f_1$	3.65	5.04	34.	
Datolite	$(ca_2\ si_4\ b_3)\ o_9 + 1\ aq$	2.99	5.35	37.5	forms coating of $Ca\ F_2$.
Prehnite	$(ca_2\ al_3\ si_6)\ o_{12} + 1\ aq.$	2.95	5.64	43.6	slightly attacked.
Talc	$(mg_4\ si_{10})\ o_{14} + 1\ aq$	2.60	6.07	62.8	
Ripidolite	$(mg_5\ al_3\ si_6)\ o_{14} + 4\ aq.$	2.70	5.70	31.3	
Margarite	$(ca_1\ al_6\ si_4)\ o_{11} + 1\ aq.$	2.99	5.54	30.	

To the above may also be added the non-silicate species corundum, spinel, and chrysoberyl, which are not attacked, and the artificial product glass, which is.

I have included in both classes several species which seem to be on the border line, and which sometimes seem to be unattacked, while at other times, by longer exposure or by treatment of a different surface, a slight action becomes evident. Thus with vesuvianite the prismatic faces of a crystal showed no etching, while the basal plane of the same crystal was perceptibly attacked ; this, however, might have been due to a difference in the time of exposure, though in other cases, as in quartz, it is undoubtedly the fact that some surfaces are not attacked as readily as others.

By inspection of the data given it will be seen that the amount of silica present does not determine the action of the acid, nor does the molecular ratio of silica to the bases, but we see that the volumes show a very decided difference. In the non-attacked species the volume for the greater number is considerably below 6, while in the non-resisting species it is generally considerably above this figure. Thus comparing enstatite and diopside with wollastonite and tremolite, we have in the first two the volumes of 5.54 and 5.48, in the less dense wollastonite the volume is 6.62, while the tremolite has an intermediate volume of 5.88, and it is likewise intermediate in its relation to the acid. These four minerals differ in composition mainly by the gradual substitution of lime for magnesia, the ratio of bases to silica remaining unchanged. It is possible that the nature of the base may have a considerable effect on the extent of condensation of the molecule. In the above instances the replacement of magnesia by lime seems to tend to increase the volume and diminish the power of resistance to HF.

At the suggestion of Dr. T. Sterry Hunt, while carrying on these qualitative tests, I also proceeded to make quantitative comparisons of several minerals. I proposed to use quartz as a standard of reference, but immediately found that it was so slightly attacked that it would not do for the purpose.

In these experiments the minerals were reduced to an average size of 3-100 cubic millimeter by careful sizing, and one grm. of each sample was taken for each experiment. The samples were all treated for one hour with an excess of dilute hydrofluoric acid (9%), at the ordinary temperature of the laboratory, all conditions being, as far as possible, the same. At the expiration of that time the acid was poured off, the residues carefully washed and dried, and where any insoluble fluorides or products resulting from the decomposition of the mineral were present they were removed by the use of a fine bolting cloth before weighing the residue of unattacked mineral. The results obtained are given in the following table, which also shows the atomic formula, the density, the volume, and the % SiO_2 for each mineral.

QUANTITATIVE RESULTS.

	ATOMIC FORMULA.	Sp. Gr.	Volume.	% SiO_2	% Dissolved.	
Quartz	$si_1\ o_1$	2.67	5.62	100	1.56	
Tremolite	$(mg\frac{3}{4}\ ca\frac{1}{4}\ si_2)\ o_3$	2.97	5.88	57.4	2.47	Governeur, N. Y.
Augite		3.30	....	....	2.61	Note 1.
Hornblende		3.21	....	....	2.64	
Chrysolite	$(mg_1\ si_1)\ o_2$	3.40	5.38	45.	5.40	
Prehnite	$(ca_2\ al_3\ si_6)\ o_{11}+1\ aq$	2.95	5.64	43.6	8.59	Paterson, N. J.
Albite	$(na_1\ al_3\ si_{12})\ o_{16}$	2.62	6.24	68.6	23.1	
Labradorite	$(ca\frac{3}{4}\ na\frac{1}{4}\ al_3\ si_6)\ o_{10}$	2.70	6.28	55.5	24.65	Note 2.
Petalite	$(li_1\ al_4\ si_{20})\ o_{25}$	2.42	6.33	78.	28.97	Sweden.
Oligoclase	$((h\ ca)\ \frac{1}{4}\ na\frac{3}{4}\ al_3\ si_{10})\ o_{14}$	2.61	6.41	64.26	35.25	Haddam, Ct.
Orthoclase	$(k_1\ al_3\ si_{12})o_{13}$	2.54	6.83	64.6	43.45	Pike's Peak, Colorado
Iolite	$(mg\frac{2}{3}\ fe\frac{1}{3}\ al_3\ si_5)\ o_9$	2.67	6.31	49.	47.34	Finland, Note 3.
Oligoclase	$(na\frac{3}{4}\ ca\frac{1}{4}\ al_3\ si_9)\ o_{13}$	2.65	6.27	61.5	50 83	Sweden.
Nephrite		....	....	....	61.59	Easton, Pa., Note 4.
Leucite	$(k_1\ al_3\ si_8)\ o_{12}$	2.56	7.09	55.	66.30	
Rhodonite	$(mn_1\ si_2)\ o_3$	3.63	6.06	46.7	69.21	Franklin, N. J.
Opal	$si_1\ o_1$	2.2	6.81	100.	77.28	
Serpentine	$(mg_3\ si_4)\ o_7+2\ aq$	2.53	5.78	42.	80.67	
Halloysite	$(al_3\ si_4)\ o_7$	2.40	5.75	43.3	100.0	Lookout, Ala., Note 5.
Willemite	$(zn_1\ si_1)\ o_2$	4.18	6.63	27.5	100.0	Franklin, N. J.

Two samples of willemite were also treated for 15 minutes with the following results :

Green Willemite, massive	86.78
Brown " crystallized (Troostite)	92.09

NOTE 1.—These samples of augite and hornblende are from Teplitz, Bohemia. I have not their analysis.

NOTE 2.—The surfaces of the grains were coated with a white incrustation, probably of calcium fluoride, which would both retard the action of the acid and make the apparent amount dissolved less than the truth ; both causes of error acting in the same direction.

NOTE 3.—A fine powder insoluble in HF was formed—either an insoluble fluoride or an included mineral.

NOTE 4.—This so-called nephrite, said to be a variety of amphibole, is from Easton, Pa. Dana says it is a mixture of minerals. The result I have obtained shows that it is certainly not amphibole, nor does it contain much, if any, of that species.

NOTE 5.—This disintegrated with great rapidity, but left an insoluble residue behind, either an insoluble product of the reaction or an included mineral.

Now, on comparing together minerals of like formula in this table, we see that the one with least volume is likewise least attacked by the acid, for instance, quartz and opal, tremolite and rhodonite, chrysolite and willemite, albite and orthoclase. Taking together the different felspars and minerals of analogous composition, although they are not strictly comparable on account of the variation in the amount of silica, we have the following series in the order of solubility : albite, labradorite, petalite, oligoclase, orthoclase, oligoclase, leucite ; which, with the exception of the second oligoclase, is also the order of increase of volume. It is, of course, to be expected that variations in composition will have a great influence in modifying the action of the acid, but oligoclase seems to be exceptional, as it is intermediate in composition between albite and labradorite, and we should expect its solubility to be between them also.

The oligoclase which gave me a solubility of 50.83% was from a Swedish locality, but I could not obtain its analysis. On account of the discrepancy in this result, when compared with what we should expect, I obtained from Prof. B. W. Frazier, of Lehigh

University, a sample of oligoclase from Haddam, Conn. (the first one in the table), which gave a solubility of 35.25%, a specific gravity of 2.61, and a volume of 6.41. The analysis of oligoclase from this locality (Dana's System, p. 347), leads to an atomic formula differing slightly from that given by Dr. Hunt, but agreeing with that given by Dana. This result takes its place in the proper order according to volume and, I think, leaves no doubt that the volume accorded to the 50.83% oligoclase is erroneous. This experiment was made at a different time and under slightly different conditions, so that the solubility found is probably rather less than it should be.

To further illustrate the subject, I obtained a sample of slag from an iron cupola furnace, the outside portion being vitreous from sudden cooling while the interior was opaque and crystalline. The composition of the two portions being presumably the same, as the piece chosen was but the size of the first, any variation in solubility could only be ascribed to the molecular condition and not to any difference of composition. The crystalline portion was very porous, it having an apparent specific gravity in the lump of 2.34, but on pulverizing finely, though not to an impalpable powder, the density rose to 2.97. The vitreous portion changed less, from 2.77 in lump to 2.81 in powder.

The results obtained for solubility in 9% acid were:

	Sp. Gr.	Volume ratio.	Per cent. dissolved.
Vitreous slag....................	2.81	1.057	68.80
Crystalline slag................	2.97	1.	9.60

This result also agrees perfectly with what might be expected.

M. W. Iles, in a paper on "The Decomposition and Analysis of Slags,"* describes a method of obtaining samples of slags for analytical purposes by chilling the melted slag suddenly, thus obtaining a vitreous sample which is readily soluble in dilute hydrochloric acid; while if allowed to cool and become crystalline, it is not attacked by the acid. This is a practical application of the law of increase of solubility with increase of volume set forth

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* School of Mines Quarterly, Vol. 5, p. 351.

by Sterry Hunt in 1863, when he asserted, in comparing the silicates meionite and zoisite, that "the augmentation of hardness, of density and of chemical indifference which is seen in this last species is doubtless to be ascribed to a more elevated equivalent; or, in other words, to a more condensed molecule." Again, in 1867, he wrote, after naming a number of groups of related minerals: "The hardness of these isomeric or allotropic species, and their indifference to chemical reagents, increases with their condensation; or, in other words, varies inversely as their empirical equivalent volumes, so that we here find a direct relation between chemical and physical properties." This is resumed in his concise statement that "in related and homologous species, the hardness and chemical indifference are inversely as the value of V (the so-called atomic volume); or in other words, that they increase with the diminution of V."* The specific gravity of solids and liquids is, according to Sterry Hunt, a function of their equivalent weights.

In order to test still further the truth of this law, I ignited several samples of the granulated quartz, used in the previous experiments, for varying periods of time, anticipating that the longer the period of ignition the greater the solubility would be, since we know that fused quartz has a lower specific gravity than the original crystal. The results were extremely satisfactory, and are as follows:

INFLUENCE OF IGNITION ON THE SOLUBILITY OF QUARTZ.

One gram of each sample treated for one hour with excess of dilute (9%) HF.

	Per cent. dissolved.	Sp. Gr.
Raw quartz	1.28–2.18	2.64
Same, ignited over Bunsen burner 30 minutes	1.61	
" " " " " 45 "	1.78	
" " " " " 75 "	1.87	
" " " " " 120 "	2.05	
" " " " " 75 " and over blast lamp 45 minutes	4.23	2.62
" " " blast lamp 120 "	2.79	
" " " " " 210 "	5.35	
Fused quartz	11.02	2.22

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* Comptes Rendus de l'Académie des Science, lvi., 1256; Hunt's Chemical and Geological Essays, pp. 446, 457; and Mineral Physiology and Physiography, p. 304.

I obtained the sample of fused quartz through the kindness of Dr. T. Sterry Hunt, who prepared it in the electrical furnace of the Messrs. Cowles, at Cleveland, September 1st, 1885.* The sample used was reduced to the same size as in the other experiments and, in that form, had a specific gravity of 2.22. It was treated with the dilute acid for an hour and a quarter, a sample of ordinary quartz being simultaneously treated for comparison. In that time it had lost 13.77%, against 2.13% for the raw quartz. In the table I have deducted one-fifth these amounts, so as to give the solubility in one hour, which permits direct comparison with the other determinations. The solubility of the raw quartz varies in different determinations; I have in all obtained the following values: 1.28, 1.56, 1.70, 1.70, 2.18. The last figure is probably too high—from mechanical loss.

Although the temperature of ignition is far too low to effect fusion, the results show that a molecular change has commenced towards the less dense and more easily soluble form of silica. In this connection, I attempted to prepare some artificial tridymite by the fusion of amorphous silica with sodium metaphosphate and obtained thin plates which were readily soluble in the acid. I had not enough material to make other than the one test, and only surmise that it really was tridymite, though probably an impure sample.

The action of quartz being so interesting, I made several experiments on whole crystals of different crystalline modifications from three localities, in order to ascertain the quantitative differences between them, since I had noticed in my qualitative tests that some quartz crystals did not show any appreciable etching action. As in these cases the amount of action depends on the surface exposed, I have measured the area of the exposed faces, protecting broken surfaces and certain faces, with wax, unless otherwise mentioned.

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* Transactions American Institute of Mining Engineers, Vol. XIV., p. 492.

TREATED FOR ONE HOUR IN 9 PER CENT. HYDROFLUORIC ACID.

	Locality.	Weight. Grams.	Amount Dissolved.		Area of Faces. Square Centimeters.	Amount Dissolved per Square Centimeter. Grms.	Remarks.
			Total.	Per Cent.			
Quartz Crystal.	Herkimer, N Y..	0.5742	0.0002	0.035	1.5	0.000133	Not visibly etched.
Opal...........	....	0.4005	0.1140	28.46	1.5	0.076	Approximately same size.

With opal, the figure given as expressing the amount dissolved per square centimeter is necessarily lower than the truth, as the area of the exposed surface diminishes as the solvent action progresses. In the present case, the area at the end of the experiment is only about 80 per cent. of the area at the commencement, so that the loss per square centimeter will be somewhere between 0.095 and the figure given. The quartz crystal was without flaw, and was exposed on all faces ; it did not show the slightest dimming of its brilliancy, and were it not for other experiments, it would be difficult to believe that the loss observed was not due to errors of experiment solely.

CRYSTALS OF QUARTZ.

Treated for 1 hour in Concentrated (54 per cent.) HF.

Locality.	Weight. Grams.	Amount Dissolved.		Area of Faces. Sq. Cm.	Amount Dissolved per Sq. Cm. Grms.	Remarks.
		Total.	Per Cent.			
Herkimer, N. Y......	0.9733	0.0004	0.041	2.2	0.000182	Not visibly etched, perfect crystal, completely exposed.
White Plains, N. C...	0.6805	0.0016	0.235	....	....	Visibly etched, fractured surface also exposed.
White Plains, N. C...	6.5827	0.0024	0.036	7.2	0.000333	Visibly etched, acute rhombohedral faces exposed.
Hot Springs, Ark.....	22.0087	0.0050	0.023	11.9	0.000446	Visibly etched, prismatic faces exposed.

These figures show a quite decided, though small, difference of susceptibility in the crystals from different localities. In the first "White Plains, N. C.," specimen, the amount dissolved was relatively larger than in any of the others, but this is due to the exposure of the fractured surface, which is far more readily attacked than the natural faces, as the following experiments will show :

ACTION ON POLISHED SECTIONS OF QUARTZ CUT PERPENDICULARLY TO THE AXIS OF THE CRYSTAL.

Treated for 1 hour in 54 per cent. HF.

Total Area Exposed. Square Centimeters.	Weight. Grams.	Amount Dissolved.		Amount Dissolved per Square Cm. Grms.
		Total.	Per Cent.	
13.73	2.5242	0.0575	2.28	0.0042
15.24	2.2259	0.0778	3.49	0.0051
12.46	6.3890	0.0540	0.84	0.0043

In the last case, the natural faces of the crystal formed the sides of the section, and, if we exclude them from our calculations, the area of the *cut* surfaces will be 8.46 sq. cm., and the amount dissolved per square centimeter of cut surface will be 0.0064. Here we see that the rate of attack is from 10 to 30 times greater than on the natural faces.

The etched surfaces of quartz crystals show a very peculiar variety of markings. Irregular and curved hair lines, having apparently no relation to the crystallographic form, are found in some places; the twinning structure is also developed, showing the complex nature of the crystal. On artificial surfaces of quartz, the twinning structure is made very evident. In 1852–1855, F. Leydolt* made a series of experiments on quartz and agates with hydrofluoric acid, and says: "I am led to believe * * * that agates * * * are composed of layers of different chemical constitution, or at least in a different state of aggregation. * * * Quartz crystals preserve their brilliant surface, and are not dissolved." He also says: "The felspar is dissolved, while the quartz remains quite unaltered;" and again: "Wood opals and other quartzose stones show differences in constitution."

The action of hydrofluoric acid on different silicates has already been utilized as a means of purification,‡ and for the proximate

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* Eine neue Methode, die Achate und andere quartzhältige Mineralien naturgetreu darzustellen. Jahrb. d. K. K. geologischen Reichsanstall, II. Jahrgang 2, S. 124.

† Loc. cit., S. 126.

‡ Treatment and Qualitative Composition of Zircon. Ed. Linnemann. Chem. News. p. 233. Vol. LII. 1885.

analysis of rocks, * but, so far as I am aware, it has only been used to separate the insoluble or difficultly soluble minerals from the readily soluble ones, with which they are associated. From the quantitative results presented in this paper, it will be readily seen how it may be applied to determine the nature of a mineral; to distinguish, for instance, between the different felspars. It would also be possible to arrive quickly at the approximate composition of a rock, of which the constituent minerals were known, such as a syenite or granite. When used in cônjunction with Thoulet's solution, complex mixtures of minerals may be readily determined. I applied the acid to determine whether a specimen of cassiterite and quartz was only a mixture of the two minerals or a silicate of tin, as was claimed for it by its European label. I obtained a residue of pure SnO_2, practically the whole amount present, which in all probability, would not have been the case if it had been a compound.

Of course, the figures given in the present paper apply only to the circumstances under which the experiments were carried on ; it is possible that, with a different degree of comminution, or with a different strength of acid, the rate of attack might be different, so that each investigator would need to construct a table of solubilities suited to the circumstances under which he works.

Many analytical processes have been proposed, and used, either for the decomposition of silicates by hydrofluoric acid, or for the determination of fluorine by conversion into silicon fluoride. Now, it is plain that, in the latter case, quartz is about the worst material we can introduce to furnish the necessary silica ; and, in the former case, that we cannot depend on the complete decomposition of a silicate by simple treatment with hydrofluoric acid.

In conclusion, I desire to acknowledge my indebtedness to Dr. T. Sterry Hunt for many suggestions which he has made, and information given, during the course of my experiments ; to Dr. T. Egleston for his kindness in furnishing me with most of the material for the investigation ; and to Prof. B. W. Frazier and Mr. G. F. Kunz for assistance in procuring special specimens.

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* Minéralogie Micrographique. F. Fouqué et Michel Levy. Paris, 1879. p. 116, and Sterry Hunt, Mineral Physiology and Physiography, p. 214.