

XXXII.—*On two New Processes for the detection of Fluorine when accompanied by Silica ; and on the presence of Fluorine in Granite, Trap, and other Igneous Rocks, and in the Ashes of Recent and Fossil Plants.* By GEORGE WILSON, M.D.

(Read April 19, 1852.)

In several communications made to this Society and to the British Association, I have announced the results of a series of observations on the distribution of Fluorine throughout the mineral, vegetable, and animal kingdoms. To myself, the least satisfactory part of these investigations has been the inquiry into the presence of fluorine in plants, for I have been more frequently foiled than successful in my attempts to detect it in them. Others have not, apparently, been more successful. DAUBENY was as unable as SPRENGEL at an earlier period had been, to obtain evidence that the element under notice is present in vegetable structures ; and WILL of Giessen, the discoverer of fluorine in plants, speaks only of “traces” of it having been detected in barley. Later observers have not spoken more confidently concerning its abundance in vegetables ; and in the many analyses of the ashes of plants which have recently been published, it seldom, if ever, finds a place.

That one cause of this apparent rarity of fluorine in vegetables, is the small extent to which it occurs in them is certain ; but I have never doubted that the chief reason why it appeared to be so scanty a constituent of plants, was its occurrence along with silica, which makes its recognition very difficult. I had given up, accordingly, all hopes of satisfactorily demonstrating its wide distribution, till better processes than are at present in use, were devised for its detection when accompanied by silica.

For the same reason I have thought it hitherto useless to endeavour to trace back fluorine from the plants, animals, natural waters, and more accessible strata which are the main seats of life at the present day, to those earlier rocks and geological formations which have furnished our soils, and have contributed the chief soluble matters which are found in the lakes, rivers, and seas of the globe. The more ancient rocks abound in silica, and, with our present processes, the prospect of discovering fluorine in trap and similar siliceous masses, was not encouraging. A representation, however, from Professor JAMESON, as to the importance attaching to the detection of fluorine in the most ancient rocks, led me to reconsider the geological and mineralogical interest which the inquiry possessed ; and within the last six weeks I have put in practice two methods of investigation, which I shall now explain.

The processes at present in use for the separation of fluorine from silica, are in many respects satisfactory ; but they imply the rejection of glass apparatus, and the use of vessels of platina, which, from their costliness, cannot be employed of any considerable size, and, from their opacity, render the observation of phenomena occurring within them impossible. They are thus inadmissible for operations where large quantities of material must be dealt with ; and to the impossibility of employing glass and porcelain vessels, must be largely attributed the comparatively limited extent of our information as to the distribution of fluorine.

The following processes, which, in the meanwhile, are offered only as qualitative (although I hope to succeed in rendering the second of them quantitative), may be carried on in the ordinary glass and porcelain vessels of the laboratory, and admit of everything visible being observed. They are applicable to all siliceous compounds or mixtures containing fluorine, provided it be present in the form of a fluoride which admits of decomposition by oil of vitriol at its boiling point. The first stage of the process consists, in both cases, in heating the silicated fluoride in a flask along with strong sulphuric acid, so as to occasion the evolution of the fluoride of silicon,  $\text{Si F}_3$ . This gas is conducted by a bent tube into water, where it deposits a portion of gelatinous silica ; and the liquid, after filtration (which, however, is not essential), is treated as follows :—

In the first process, I adopted one of BERZELIUS' well-known methods for the isolation of silicon. The filtered liquid was neutralised with potass : and the resulting gelatinous precipitate of fluoride of silicon and potassium ( $2 \text{ Si F}_3 + 3 \text{ KF}$ ), after being washed, was dried, and transferred to a small metallic crucible, in which it was heated with potassium, so as to separate and set free the silicon, and convert the whole of the fluorine into fluoride of potassium. This fluoride was then dissolved out by water, evaporated to dryness, and treated in the ordinary way with oil of vitriol, so as to evolve hydrofluoric acid, which could be made to record its evolution by the etching which its vapour occasioned on a plate of waxed glass, with lines written on it through the wax.

This process is necessarily tedious, and is liable to several objections. The most serious of these is the impossibility of effecting the complete decomposition of the fluoride of silicon and potassium, by potassium, so as to liberate the whole of the silicon ; and the risk of the latter undergoing oxidation into silica during the washing of the ignited mass. Accordingly, though this method gives good results, and has enabled me to detect fluorine in coal, in which I could not previously detect more than the faintest traces of it, yet it almost unavoidably necessitates a loss of the element in question, and is much inferior in simplicity and certainty to the process which I am about to describe.

In the second process, as in the first, the substance under examination is heated with oil of vitriol so as to yield fluoride of silicon, which is conducted into water. The resulting solution (with or without filtration) is neutralised with

ammonia instead of potass, and then evaporated to dryness, which has the effect of rendering the silica produced insoluble. On digesting water on the residue, fluoride of ammonium is dissolved, and the solution requires only to be evaporated to dryness and moistened with sulphuric acid to give off hydrofluoric acid, which readily etches glass. The stages in the ammonia process are thus :—

1st, Distillation of the substance with oil of vitriol, so as to produce fluoride of silicon,  $\text{Si F}_3$ .

2d, Neutralisation of the aqueous solution of the distillate, with ammonia in excess, so as to produce fluoride of silicon and ammonium,  $2 \text{Si F}_3 + 3 \text{NH}_4 \text{F}$ .

3d, Evaporation of the neutralised liquid to dryness, so as to separate silica, and render it insoluble.

4th, Exhaustion of the residue with water, and evaporation to dryness, so as to leave fluoride of ammonium.

5th, Moistening of the ammonio-fluoride with oil of vitriol, so as to liberate hydrofluoric acid; which will act upon glass.

I have tried this process with Aberdeen and Peterhead granite; with three trap rocks from the neighbourhood of Edinburgh, namely, basalt from Arthur Seat, greenstone from Corstorphine Hill, and clinkstone from Blackford Hill; with a deposit from the boiler of the Atlantic steamer, Canada; with a fossil bone; with the ashes of charcoal, of barley-straw, and of hay; and in all with such success that the applicability of the process to the end proposed is certain. The pieces of glass, etched by hydrofluoric acid evolved from the substances referred to, which I lay upon the table, are not selected successful specimens, but represent the whole of the trials made by the ammonia process. The etchings on the majority of them are as deep as could be obtained from pure fluorspar and oil of vitriol; and, with the experience which I have now acquired, I have no doubt that I shall be more successful in succeeding trials with vegetable ashes, which, for reasons to be presently mentioned, require more precautions than fragments of rock do.

The examination of a hard crystalline mineral, such as granite, or an unweathered trap, presents no difficulties. It must be reduced to a tolerably fine powder, and employed in considerable quantity. A little sulphurous acid is always evolved during the action of the oil of vitriol, from the dust which is gathered during a protracted process of powdering; but the presence of this acid in small quantity is of no importance, and the powdering of the rock is the most troublesome part of the investigation.

It is otherwise with weathered granite and trap, which contain chlorides and carbonates, and give off hydrochloric and carbonic acids when treated with sulphuric acid. These gaseous acids materially interfere with the processes described by the frothing which they occasion, and by their tendency to sweep away the hydrofluoric acid which may accompany them. In my earlier trials, accordingly,

I treated the powdered pieces of rock with hydrochloric acid, and washed them with water, then dried them, and heated them with oil of vitriol. The preliminary treatment, however, risked, and I have no doubt occasioned, the loss of the fluorides present in the mineral, which were soluble in water or in hydrochloric acid; and latterly I abandoned this process. I refer to it here only because it explains certain of the less perfect etchings which are exhibited.

In later trials, a simpler and more satisfactory process has been put in practice. The powdered rock has been added to oil of vitriol in the cold, in small quantities at a time, so as to prevent any great rise in temperature. So long as the heat evolved is not considerable, there is no risk of fluorine escaping, either as hydrofluoric acid or as fluoride of silicon, whilst any chlorides or carbonates present are decomposed, and the hydrochloric and carbonic acids evolved, are carried away, before their escape can interfere with the evolution of fluorine. When the oil of vitriol is afterwards raised to its boiling-point, the fluoride of silicon is liberated, and little difficulty attends its collection and identification.

The ashes of plants are somewhat less easily examined. They almost invariably contain charcoal, which occasions the evolution of sulphurous acid with hot oil of vitriol. Sulphurous acid, however, does not very materially interfere with the detection of fluorine, as it can be expelled by heating the distillate before adding ammonia, which is the process I have hitherto generally followed. It may also be converted into sulphuric acid by the cautious addition of nitric acid, and then its presence is quite immaterial. But in several quite successful trials no steps were adopted to separate the sulphurous acid.

The specimen laid upon the table, of glass etched by fluorine from barley-straw, will illustrate the applicability of the process to plant-ashes largely charged with silica, and which yielded, with oil of vitriol, carbonic and hydrochloric acid, besides much sulphurous acid.

The glass etched by the fluorine of charcoal-ashes is still more deeply corroded, although they were subjected to no preliminary process to remove the volatile acids which they contained, or to set free or separate the sulphurous acid which they yielded.

In truth, the ammonia process has succeeded with every substance upon which I have tried it. The worst result has been with the ashes of hay, but they had been washed with water and hydrochloric acid to remove chlorides and carbonates; and in former papers I have shewn that such washings remove fluorides. Notwithstanding this, the evidence of the presence of fluorine in hay, afforded by the specimen, is such as has not hitherto (so far as I am aware) been afforded by any analyst, and the omission of the washings will, I have no doubt, yield a still more satisfactory result on a repetition of the analysis. The same remark applies to coal-ashes, by the fluorine of which I have only one etching to shew. It is not a favourable specimen; the ashes were washed with a considerable volume of

hydrochloric acid and water; the product of distillation was tested by the less perfect potassium-process; and the lines etched by the hydrofluoric acid were drawn too fine. Experience has taught my assistants that the wax should be spread thin, and the lines through it be made with a broad point, if a distinct etching is to be obtained. But, withal, the results with coal-ashes are sufficiently marked.

I have further tested the sufficiency of the ammonia process in the following stringent way. A fossil bone from the Himálayas, which I had already ascertained to contain a fluoride, and which was full of crystals of carbonate of lime, was reduced to powder, and mixed with powdered glass so as to add to it excess of silica. It was then subjected to the ammonia process, and has yielded an etching as deep as the purest fluorspar could have given with oil of vitriol.

The result is so marked, that I should recommend the deliberate addition of silica to bodies suspected to contain fluorine, as a provision for permitting such substances to be analysed in *glass* vessels, in which the largest quantities may be subjected to examination without risk of missing the element in search, or permitting it to escape.

Five points call for further notice.

1st, When a silicated fluoride, as I may, for the sake of brevity, call it, is distilled with oil of vitriol, the whole of the fluoride of silicon comes away as gas, as soon as the oil of vitriol has reached its boiling-point. It is not necessary, accordingly, to subject a body supposed to contain fluorine to any lengthened ebullition; and, in the case of plant-ashes, it is desirable to arrest the boiling as soon as all the fluorine has been evolved, for protracted ebullition only occasions evolution of sulphurous acid. Besides the ultimate glass-etching, the escape of fluorine is rendered manifest by the appearance of a white gelatinous body in the water, through which the gas evolved ( $\text{Si F}_3$ ) is passed; and by the production of a gelatinous, flocculent precipitate, when the solution of this gas is neutralised with potass. The coal-ashes gave all those results.

2d, It appears exceedingly probable, that much of the silica occurring in the forms of quartz, chalcedony, opal, sinter, and the like, which is generally supposed to have been deposited from aqueous or alkaline solution, has owed its origin to the decomposition of fluoride of silicon by water, or has otherwise been related to fluorine as its solvent or transferring agent. This, or rather the less precise notion of fluorine conveying silica, has been suggested by my friend Mr A. BRYSON, and by Dr H. BUCHANAN, E.I.C.S.

3d, The occurrence of fluorspar in drusy cavities in greenstone, along with silica, as in the specimens obtained from Bishopton, on the Clyde; the similar occurrence of apophyllite in the cavities of trap; the association of topaz, pycnite, lepidolite, and most of the other compound fluorides, with granite, gneiss,

and mica slate, will acquire additional significance from the discovery that fluorine occurs in the rocks which form their matrices.

*4th*, The presence of fluorine in plants is now rendered doubly probable, as it may enter them alike in combination with a metal such as potassium, sodium, or calcium, or in association with silica.

*5th*, The presence of fluorine in animals may now be fully accounted for; as it not only enters their bodies in the water they drink, but is contained in the vegetable food, by which, directly or indirectly, the whole animal kingdom is sustained. The prosecution of these views, however, will be taken up in succeeding papers.