

*Chemical Analysis of the Meteoric Stone found at Makariwa, near  
Invercargill, New Zealand, in the year 1879.*

By L. FLETCHER, M.A., F.R.S.,  
Keeper of Minerals in the British Museum.

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1. **A**S the preliminary examination of the Makariwa stone had already indicated to Professor Ulrich<sup>1</sup> the presence of mineral constituents having the physical characters of olivine, enstatite, glass, a substance resembling glass, nickel-iron, troilite, magnetite, hydrous oxide of iron, and possibly chromite, the quantitative chemical analysis presented obvious difficulties, among which may be specially mentioned the fact that one chemical element (iron) enters into the composition of each of the above fine-grained and closely intermingled constituents. This chemical examination I was invited to undertake by Professor J. W. Judd, F.R.S., through whom the two fragments of the stone sent to this country by Professor Ulrich have been generously presented to the British Museum.

A few words relative to the methods which experience has suggested to mineralogical chemists for the solution of this kind of problem will be of service to others who may hereafter be called upon to undertake such an investigation.

PART I.—METHODS OF METEORITIC ANALYSIS.

2. *Extraction of the nickel-iron.* In the classical research of Mr. Edward Howard<sup>2</sup> on the composition of the stones reported to have fallen at Siena, Wold Cottage, Krakhut and Tabor, respectively, a research which established for the first time not only the close similarity of those stones to each other, but also their difference from any terrestrial rocks then known, the magnet was already (1802) employed for the extraction of the nickel-iron, and hydrochloric acid and nitro-hydrochloric acid for the separation of the residual unattracted powder into different kinds of

<sup>1</sup> *Proc. Roy. Soc.*, 1893, vol. 53, p. 54.

<sup>2</sup> *Phil. Trans. Roy. Soc.*, 1802, p. 168.

material. Some analysts, as for instance Proust (1806) in the examination of the Sigena stone, have kept the powdered material under alcohol during the magnetic separation; others, as Berzelius (1834) in the examination of the Blansko meteorite, have replaced the alcohol by water: but neither variation has met with favour among chemists owing to the increased liability of the finer particles of the nickel-iron to become oxidised during the operation. The magnetic method of separation is, however, far from perfect, for a noteworthy proportion of non-metallic material adheres to the extracted nickel-iron.

3. Various attempts have been made by chemists to discover a solvent for the nickel-iron which is without effect on the silicate decomposable by hydrochloric acid: and after aqueous solutions of chlorine, iodine, and bromine had been in turn rejected, Wöhler suggested the use of cupric chloride, though this involved the introduction of a large proportion of non-volatile foreign matter into the analysis. Later, it was pointed out by Rammelsberg (1870) that an excellent substitute for this reagent is provided by a solution of mercuric chloride, such as had been already employed by Boussingault (1868) in his method of isolation of the carbon of artificial iron; the use of mercuric chloride being advantageous both by reason of the volatility of mercury compounds and because of the slowness of its action on the troilite (ferrous sulphide), schreibersite (phosphide of iron and nickel), and the silicates of meteoric stones.

4. More recently still (1888), it has been pointed out by Friedheim<sup>1</sup> that the action of mercuric chloride on the latter minerals can be even further reduced by the addition of ammonium chloride to the solvent liquid. He recommends the use of a solution containing 12 grams of the double salt ( $\text{HgCl}_2, 2\text{NH}_4\text{Cl}, 2\text{H}_2\text{O}$ ) to the litre: the solution being freshly prepared, boiled to expel the dissolved air, and used cold. Further, to prevent the formation of insoluble oxychlorides of iron (containing also nickel), the action of the mercuric solution is allowed to take place either in a strong flask from which the air has been extracted or in an atmosphere of hydrogen.

5. *Separation of the silicates by means of hydrochloric acid.* The separation of the silicates from each other by means of hydrochloric acid is likewise imperfect; it has been demonstrated by various chemists that in this operation there is a very appreciable action on the enstatitic ingredient of a meteoric stone. However the operation is conducted, some of the enstatitic ingredient passes into solution; the only question is

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<sup>1</sup> *Sitz. Ak. Berlin*, 1888, p. 345.

how much; the amount depends on the strength of the acid, the temperature, and the length of time during which the action is continued. Unless precautions are taken, the bases of the greater part of the enstatite may pass with those of the olivine into solution, or on the other hand much of the olivine may be left undecomposed among the enstatitic residue; in one case, for example, an experienced mineralogical analyst has suggested that no less than 21 per cent. of undecomposed olivine were still present in the material which remained to him after the action of the acid. Nor is it practicable to attempt to continue the action until there is no longer a noteworthy amount of silicate being decomposed.

6. The most satisfactory results appear to be obtained when (1) the dilute hydrochloric acid has a specific gravity of 1.06; (2) the action is allowed to take place on the water-bath; (3) to last for two hours, and without much variation in the volume of the acting liquid; and (4) is repeated once or twice after decantation of the products of the preceding extraction.

7. *Determination of the silica of the decomposed silicate.* The greater part of the silica of the decomposed silicate remains with, and must be extracted from, the undecomposed residue: this is effected by boiling the residue, while still moist, with a solution of sodium carbonate, to which sometimes caustic soda is added. My former colleague, the late Dr. Flight, showed that there is an appreciable solvent action by caustic soda on the enstatitic residue itself, and discouraged its use: on the other hand, the addition of the caustic soda is intended to secure the complete removal of the liberated silica, while Rammelsberg himself long ago (1848) pointed out that there is already a perceptible solvent action on the residual silicate, even on boiling with a simple solution of sodium carbonate, and attributed it to the presence of undecomposed olivinic silicate. The rest of the silica is obtained by evaporating the hydrochloric acid extract to dryness.

8. *Determination of the troilite, schreibersite and chromite.* If the sulphur be wholly present in combination with iron as troilite ( $\text{FeS}$ ), and the phosphorus wholly in combination with iron and nickel as schreibersite ( $\text{Fe}_2\text{NiP}$ ), the proportions of these mineral constituents can be calculated as soon as those of the sulphur and phosphorus have been determined. The chromite being unacted upon by the hydrochloric acid, remains with the enstatitic residue, and can be weighed after removal of the latter by help of hydrofluoric acid or fusion with alkaline carbonates.

9. *Determination of the alkalis.* The alkalis are best determined by direct extraction according to the method invented by the late

Professor Lawrence Smith; namely, ignition with a mixture of calcium carbonate and ammonium chloride. The action of the various reagents on the glass and porcelain vessels during a prolonged general analysis prevents the assignation of much importance to the weights of the alkalies as obtained after successive removal of the other bases, at any rate when the proportion of the alkalies in the original material is small, as in the case of meteoric stones.

10. *General order of procedure.* For such an analysis of a meteoric stone it is thus necessary (1) so to prepare the powdered material that the mixture is practically homogeneous; to use of this mixture (2) a weighed portion (say 0.5 gram) for the determination of the alkalies; (3) another weighed portion (say 1 gram) for the determination of the sulphur and phosphorus, and therefore of the troilite and schreibersite; and (4) another weighed portion (say 2 or more grams) for successive separations with mercuric solution and hydrochloric acid. In this way become known the proportions of the nickel-iron, chromite, troilite and schreibersite, and the proportion and composition of the residual silicate left undecomposed by the hydrochloric acid. Since the schreibersite, though not easily dissolved by acids, is in very small quantity and in a fine state of division, the whole of its iron and nickel will probably pass with the iron of the troilite into the hydrochloric acid extract: after subtraction of these known amounts from the total bases found in that extract, the residual bases must in general belong to the decomposed silicate, of which the silica itself has been isolated in the way above described.

11. *Case of a rusted meteoric stone.* In the case of a rusted meteoric stone, the late Professor von Baumhauer showed that by heating the powder to low redness in a current of hydrogen, the rust might be brought back to the metallic condition and then extracted with mercuric chloride, without involving any noteworthy alteration in the composition of the residual silicates.

12. *Brief sketch of the analysis of the Makariwa stone.* The above will make sufficiently clear the general plan of the following quantitative analysis of the Makariwa stone, which may be briefly summarised as follows:—

It was found advisable to make a preliminary separation by means of a magnet into attracted and unattracted material. Treatment of the attracted material with ammonio-mercuric solution revealed the fact that the proportion of magnetic oxide of iron was too large to be negligible, and indicated the necessity of reducing the rust of the unattracted

material in a current of hydrogen, and of subsequently extracting the reduced metal with mercuric solution: this prevents the unattracted oxide of iron due to rusting of the alloy from passing into the hydrochloric acid extract with the oxide of iron of the silicate decomposed by the acid. Accordingly, after the sulphur and phosphorus of the unattracted material had been determined, mercuric solution was employed both before and after heating the material to low redness in a current of hydrogen, the residual unrusted and rusted nickel-iron being thus separately removed. Analysis of the post-reduction mercuric extract showed that there had been an appreciable action on the silicate portion of the stone during the reduction. Further, it became obvious that the troilite was largely affected by the heating in hydrogen, and that the greater part of the iron of that constituent, and practically all the iron and nickel of the schreibersite, had gone into the mercuric solution. Hence determinations of the sulphur and phosphorus in the mercurialised residue were likewise made, so that the iron and nickel which had passed into the mercuric solution from the affected troilite and schreibersite might be allowed for. The mercurialised residue itself was treated with hydrochloric acid; the acid solution, the sodium carbonate and caustic soda solution, and the undissolved residue itself were then separately analysed. Further, various determinations of the alkalis were made.

PART II.—EXPERIMENTAL RESULTS OBTAINED IN THE COURSE OF THE  
ANALYSIS OF THE MAKARIWA STONE.

13. *Preparation of the material for analysis.* A fragment of the stone, available for chemical investigation, presented on one side the deeply rusted yellowish brown exterior mentioned by Professor Ulrich: another side had apparently been the face of a fissure and likewise showed a certain amount of rust, but more superficially than in the case of the side last mentioned. After this less rusted face had been scraped as clean as practicable, small fragments weighing somewhat over 15 grams were broken by means of a vice from that part of the stone which had been nearest the middle of the meteorite and appeared to be little altered. The fragments having first been crushed in a steel mortar, the whole, in small quantities at a time, was reduced to greater fineness in an agate mortar. During this operation streaks having a metallic lustre soon manifested themselves, while it was obvious that malleable particles were preventing the smooth working of the pestle: only one coarse grain, attracted by the magnet, was separated as interfering with the pulverisation. Thus there was already no doubt that metallic iron was present,

and that it was present almost entirely as particles of extremely small size. The whole of the material was again pulverised, and a second metallic grain was separated as interfering with the reduction to powder.

14. As nickel-iron generally occurs in meteoric stones, not only as particles visible to the naked eye, but also as particles of microscopic size dispersed through the silicates themselves, very fine pulverisation of the material is necessary, whether the nickel-iron is to be mechanically or chemically separated from the other constituents ; on the other hand, the presence of malleable metallic particles of appreciable size interferes with the required reduction of the other constituents to a fine powder. Hence it was decided to make a preliminary separation of the nickel-iron by means of the magnet ; and this would seem to be in most cases advisable for another reason, namely, that a powder containing grains of metallic iron of various sizes cannot be mixed in such a way as to be satisfactorily considered a homogeneous mixture.

15. To diminish the adherence of the magnetic and non-magnetic particles to each other, the powder was kept in the oven at a temperature of 90° C. for some hours. The magnet used for the separation was an ordinary compass-needle ; with this the whole material was slowly worked through in small quantities at a time ; a tedious operation for which the expenditure of 9 or 10 hours was found to be necessary.

16. When the unattracted material, in small quantities at a time, was next pulverised in the mortar, there was a sensible crunching beneath the pestle, showing how much the presence of the metallic particles had previously interfered with the completeness of the pulverisation. On a second magnetic separation, for which only 2½ hours were deemed necessary, the amount of material attracted was only about one-tenth that obtained in the first operation. After the next pulverisation the unattracted material was an impalpable powder.

17. But the separation into magnetic and non-magnetic, was clearly incomplete :—the attracted powder doubtless contained some adherent stony matter, the unattracted as certainly still contained some material like that already removed by the magnetic needle. It was impracticable, however, to push the mechanical separation farther ; still, the unattracted material was now in a state of such fine division that it could at length be regarded as a homogeneous mixture, and treatment with mercuric solution in the course of the analysis of the unattracted portion showed later (§40) that practically all the nickel-iron had been actually extracted. After transference to weighing tubes and drying at 110°C., the attracted material was determined to weigh 0·4791 gram ; the unat-

tracted material, which was reddish-brown in colour, 14.6929 grams ; making together 15.1720 grams, available for chemical analysis.

A. *ATTRACTED MATERIAL: TOTAL WEIGHT 0.4791 GRAM.*

18. *Treatment with mercuric solution.* A portion weighing 0.2471 gram (after being dried at 110°C.) was transferred to a small flask, through the stopper of which passed two glass tubes, one of them reaching nearly to the bottom of the vessel. 200cc. of the above-mentioned solution of mercuric ammonium chloride were poured in ; and the cold solvent, assisted by frequent shaking, was allowed to act in an atmosphere of hydrogen during two hours. The liquid having been decanted off, filtered, and washed with air-free water containing some mercuric solution, the material was again submitted to the action of a fresh portion of the solvent until the next morning, but without any other agitation than was caused by the slow bubbling of the hydrogen through the liquid. After decantation and filtration, the material was again submitted to the action of a further 100 cc. for three hours with frequent shaking. To ascertain whether solution of nickel-iron was still taking place, the third extract was acidified and the mercury precipitated from the boiling solution by sulphuretted hydrogen: after filtration and evaporation to dryness, the residual ammonium chloride showed an appreciable tinge of yellow. After no fewer than nine further extractions had been made and separately examined, it was seen that the last extract still contained a noteworthy proportion of colouring matter, and that the solvent effect had been virtually constant since the second or third extraction ; the slight differences depended, not on the order of the extract, but on the amount of shaking and the length of time during which the action had been allowed to take place. It was clear that one or other constituent of the attracted material was being only slowly dissolved, and that it was practically useless to push the operation farther. It was inferred from subsequent observations mentioned later (§110) that the continued extraction was due to the presence of particles of nickel-iron and metallic nickel partially protected from the mercuric solution by adherent rust (oxide of iron), which was itself quite unaffected by the solvent.

(a). *Attracted material: mercuric extract (or portion dissolved by the mercuric solution).*

19. *Sulphuretted hydrogen precipitates.* All the sulphuretted hydrogen precipitates were dried and slowly ignited in a large porcelain crucible to get rid of the mercury ; there was a small brown residue completely

soluble in nitro-hydrochloric acid. After expulsion of the nitric acid by evaporation to dryness with hydrochloric acid, the residual salt was redissolved in water slightly acidified with hydrochloric acid: sulphuretted hydrogen sent down from this solution an immediate dark precipitate: an examination of the filtrate showed that no iron had been carried down with the mercuric sulphide. The precipitate itself, after ignition in a porcelain crucible, was readily soluble in hydrochloric acid, the solution having a distinctly yellow colour: on evaporation to dryness and solution in water, a deep blue colouration was produced by ammonia, showing the presence of copper. The ammonium chloride was decomposed by evaporation with nitric acid, and the copper was afterwards precipitated by caustic soda; the ignited precipitate was oxidised with a drop of nitric acid, again ignited and weighed; the  $\text{CuO}$  thus obtained was found to weigh 0.0003 gram. As remarked by the late Professor Lawrence Smith, copper is always found in meteoric iron when carefully looked for.

20. *Sulphuretted hydrogen filtrates.* To find the average amount of the solvent action during the later stages, the first seven and the last five extracts (from which the mercury and copper had been thus removed) were severally collected together, and the two solutions were analysed separately in the following way. After the trace of sulphur had been filtered off, nitric acid was added and the solution was evaporated down on the water-bath until the beginning of the ebullition of nitrous oxide through the decomposition of the ammonium chloride: the liquid was then covered with a funnel and further heated until the ebullition had ceased: the funnel being then removed, the evaporation was continued to dryness and the nitric expelled by means of hydrochloric acid. After solution in slightly acidified water and dilution to the volume of a litre, the iron was precipitated in the usual way (after addition of sodium carbonate and acetic acid) by sodium acetate, filtered hot, and immediately washed with boiling water containing a little of that reagent: the precipitate was dissolved in hydrochloric acid and the iron re-precipitated in the same way: finally, after being once more dissolved, the iron was precipitated by ammonia and washed until free from chloride with boiling water containing a little ammonium acetate: this last wash-water was found to be quite free from both nickel and iron. After ignition of the precipitate, the greater part was reduced in hydrogen and dissolved in hydrochloric acid to determine the trace of admixed silica due to the action of the large volumes of hot diluted liquid on the containing vessels. The filtrates from the precipitations of the iron with sodium acetate were evaporated to dryness and a trace of silica removed: the nickel and cobalt were pre-



cipitated with the usual precautions by caustic soda, the nickel and cobalt being converted into higher oxides by bromine for the sake of greater facility of washing: the precipitate was weighed both before and after reduction in hydrogen: it may have contained a trace of magnesia due to the action of the mercuric solution on a minute amount of adherent silicate.

21. The following numbers were obtained:—

Extracts 1—7:  $\text{Fe}_2\text{O}_3$ —0.1666 gram.

After reduction, solution and reoxidation, only a minute precipitate of phospho-molybdate was obtained with molybdic solution: this was not weighed but on direct comparison was estimated to be about  $\frac{1}{8}$ th the corresponding precipitate obtained from 1.0693 gram of the unattracted material (§37), and three or four times the precipitate obtained from the mercurialised residue of the attracted material (§30): hence the greater part of the schreibersite of the attracted material has passed into the mercuric solution.

(Ni, Co)O—0.0308 gram.

0.0254 gram of this oxide gave on reduction 0.0192 gram (calculated 0.0200 gram), and after separation of the cobalt in the usual way by potassium nitrite, 0.0106 gram of potassium cobalt sulphate ( $2\text{CoSO}_4, 3\text{K}_2\text{SO}_4$ ) corresponding to 0.0015 gram of cobalt. Hence the nickel and cobalt are in the proportion to each other of 12 : 1.

The filtrate from the cobalt was tested for manganese which was found to be absent.

22. Extracts 8-12.  $\text{Fe}_2\text{O}_3$  —0.0082 gram.

(Ni, Co)O—0.0024 gram.

The colour of the extracts had already indicated the increased proportion of nickel.

(b). *Attracted material: mercurialised residue (or portion undissolved by the mercuric solution).*

23. The insoluble matter left on the filter contained, in addition to that portion of the original attracted material which had not been dissolved, mercurous chloride, free mercury, and also some adherent mercuric ammonium chloride: after drying, as much as possible was transferred to a weighed porcelain boat.

24. 1. *Matter which still adhered to the filter.* The filter, with its adherent matter, was slowly carbonised and ignited, the latter both before and after the addition of a drop of nitric acid.

The weight of the ignited matter was 0.0307 gram.

25. 2. *Contents of the boat.* For the removal of the foreign matter,

the boat and contents were heated in a glass tube in a current of hydrogen for half-an-hour, the temperature of the oven itself being  $280^{\circ}\text{C}$ . : after the first heating the material weighed 0.0781 gram, and was a black coke-like substance, strongly attracted by the magnet.

26. The weight only became constant after six more heatings, in some of which the temperature was raised until the mercury in the oven-thermometer began to boil, and the time of heating was prolonged to  $1\frac{1}{2}$  hours : the final weight was 0.0705 gram.

27. The substance was then transferred to a porcelain dish, covered with water, and treated with nitro-hydrochloric acid with the intention of converting any admixed phosphide into phosphate : there was an immediate effervescence, however, which suggested the presence of metal, either through reduction during the heating in the hydrogen even at the above low temperature, or through the incompleteness of the action of the mercuric solution : probably, as already mentioned, particles of nickel-iron and nickel had hitherto been partially protected from the mercuric solution by adherent rust. After evaporation to dryness and a twofold repetition of the evaporation with hydrochloric acid, there was still an insoluble residue of a darkish grey colour.

28. (a). From this some admixed liberated silica was extracted by a solution of sodium carbonate to which some caustic soda had been added, and was found to weigh 0.0086 gram.

29. (β). The small gritty insoluble residue itself weighed 0.0063 gram after ignition.

30. (γ). From the hydrochloric acid solution were obtained

(a)  $\text{Fe}_2\text{O}_3$ —0.0400 gram : after reduction, solution and oxidation, molybdic solution was added ; the slightness of the precipitate as compared with the one already mentioned, indicated that the greater part of the schreibersite had passed into the mercuric solution.

(b.)  $(\text{Ni}, \text{Co})\text{O}$ —0.0270 gram : on reduction 0.0108 gram of this oxide yielded 0.0086 gram, and the solution, after removal of the nickel by ammonium sulphide, contained some calcium, possibly, however, introduced by the action of the ammoniacal salts on the glass and porcelain vessels during the removal of the nickel.

**B. UNATTRACTED MATERIAL : TOTAL WEIGHT 14.6929 GRAMS.**

*1. Extractions with water, alcohol and ether ; residual alkalis.*

31. (a) *Extracted by water.* 0.9368 gram was boiled with 100cc. of distilled water, filtered after standing three hours, and washed ; the

filtrate, being slightly turbid, was allowed to stand, and after a perceptible settling during the night was again filtered; after standing two more days, the filtrate, which had now a volume of 250cc., was still slightly, and apparently permanently, opalescent. The filtrate was neutral to litmus paper. On evaporation to dryness, the residue, including therefore the material which had been in suspension, weighed 0.0068 gram; this was treated with boiling water which was allowed to stand over it for a time. The less soluble part adhered to the dish and weighed 0.0018 gram; it dissolved speedily in hydrochloric acid, and was found to contain silica, iron, calcium, and magnesium; this was probably the matter which had originally been in a state of suspension and had caused the opalescence.

The soluble part was found to weigh 0.0050 gram; it gave a bright yellow colour to the Bunsen flame; the spectrum, obtained with a small direct-vision spectroscope, consisted of a brilliant sodium line and perhaps a faint calcium line. Spontaneously evaporated on a watch-glass, the solution gave not only crystals simple, twinned and aggregated, all of them similar to those of gypsum, but also other less definite crystallisations; the above crystals were not readily soluble in water, but slowly dissolved when the watch-glass was kept for some time on the heated oven. The solution gave the reactions for both sulphate and chloride, and also for calcium and magnesium (in addition to the sodium already mentioned).

32. The salts in the aqueous solution may have been due to a speedy action of the boiling distilled water on the silicates of the meteorite in the presence of a sulphate (the latter due to alteration of some of the troilite), or to a similar action which may have taken place, though more slowly, while the stone was embedded in the ground.

33. (b.) *Extracted by alcohol.* The residue from which the part soluble in water had been extracted was dried, agitated with 80cc. of absolute alcohol, and allowed to stand for 24 hours; the alcohol was then decanted off and a further quantity poured on to the material and decanted; the mixed extracts were allowed to stand in a covered beaker for three days without any appreciable deposit of insoluble material being formed. After decantation, the liquid was allowed to spontaneously evaporate; the drying having been completed on the water-bath, the residue which was only doubtfully visible was found to weigh 0.0013 gram. This residue having been treated with alcohol once more, 0.0005 gram of less soluble matter adhered to the dish; the alcoholic solution was transferred to a watch-glass and was seen to have a slightly yellow tinge.

Alcohol thus extracts nothing appreciable from the powder,

34. (c.) *Extracted by ether.* The residue from the alcoholic extraction was next agitated with 80cc. of ether; the ethereal extract yielded on evaporation only a faint spot of oil-like matter, which dried very slowly on the water-bath; the residue weighed 0.0011 gram, but when treated with ether, as much as 0.0007 gram still adhered to the dish.

Hence ether is likewise without appreciable action on the constituents of the stone.

35. (d.) *Residual alkalies.* The amounts of the alkalies still remaining in the material after the extractions by means of water, alcohol and ether were determined (§73).

## 2. *Unattracted material: determination of the sulphur and phosphorus.*

36. *Sulphur.* A portion of the material weighing 1.0693 gram was covered with water and treated with nitro-hydrochloric acid, in small quantities at a time, on the water-bath: it was evaporated to dryness, again treated with nitro-hydrochloric acid, and the evaporation to dryness repeated: after expulsion of the nitric by hydrochloric acid, the residue was extracted with water to which a little hydrochloric acid had been added; to the filtrate was added ammonia until there was a permanent precipitate, then hydrochloric acid till the precipitate was again dissolved. The sulphuric acid was next precipitated by barium chloride; after purification the barium sulphate weighed 0.1730 gram.

37. *Phosphorus.* From the filtrate from the barium sulphate a great part of the iron was first removed by the method recommended by Professor Lawrence Smith—that is, nine-tenths of the acid solution were reduced by ammonium sulphite, boiled in a platinum dish until there was no longer any smell of sulphurous acid, ammonia added until there was a precipitate, then acetic acid, next the remaining tenth of the solution, and finally ammonium acetate; after being boiled for half-an-hour, the liquid was filtered: the filtrate gave no evidence of phosphorus when oxidised and tested with molybdic solution. The precipitate, which thus contains all the phosphorus and is admixed with barium sulphate, was treated with hydrochloric acid, filtered and evaporated to dryness; the residue was dissolved in a little nitric acid: ammonia was added drop by drop until the appearance of a permanent precipitate, then nitric acid until the precipitate was re-dissolved: next molybdic solution and solution of ammonium nitrate until there was 15 per cent. of the latter salt present in the liquid. The solution was heated to 80° C. and allowed to stand for 3½ hours, when the precipitate was collected and washed with ammonium nitrate solution; no phosphorus could be detected in the

filtrate. Finally, the precipitate was dissolved in ammonia and precipitated by magnesia mixture: the magnesium pyrophosphate weighed 0.0088 gram.

3. *Unattracted material: determination of the alkalis.*

38. Two determinations were made and are mentioned later (§§ 65, 70).

4. *Unattracted material: determination of the chromite.*

39. To ascertain whether or not any diamond was present, 1.1885 gram of the unattracted material was decomposed with hydrofluoric and sulphuric acids: the residue was entirely opaque, and when examined under the microscope appeared homogeneous: it consisted wholly of chromite, and weighed (1) on the filter 0.0041 gram, (2) after ignition 0.0034 gram.

5. *Unattracted material: mercuric extract (or part dissolved by mercuric solution).*

40. (a.) *Before reduction in a current of hydrogen.* 5.6880 grams of the unattracted material were submitted to the action of cold mercuric solution in a current of hydrogen for three hours: after removal of the mercury from the solution in the way already described, the extracted matter was found to be small.

In a second treatment the solvent, assisted by frequent shaking, was allowed to act for an hour, and then quietly during the night: the matter extracted was not more than  $\frac{1}{10}$ th of that obtained in the previous operation, and did not exceed that obtained in the later stages of the action on the attracted material (§18): its green colour indicated that it consisted chiefly of nickel.

The next residue, resulting from a third treatment of the material extending over four hours, was quite white. After slow ignition of the mercuric sulphide precipitates and solution of the small residue thus obtained, the filtrate from the slight precipitate produced in this solution by sulphuretted hydrogen was added to the collected extracts.

On analysis they yielded:—

SiO<sub>2</sub>— 0.0008 gram (thus showing the slowness of the action of the mercuric solution on the silicates).

Fe<sub>2</sub> O<sub>3</sub>—0.0007 gram (indicating the smallness of the amount of unattracted nickel-iron).

(Ni, Co, Ca, Mg)O — 0.0076 gram: after reduction in hydrogen this weighed 0.0060 gram, and yielded CaO — 0.0011 gram, and Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> — 0.0047 gram; the latter corresponds to MgO—0.0017 gram; the

(NiCo)O thus amounts to 0.0048 gram and corresponds to 0.0088 gram of metal.

The filtrate from the nickel precipitate obtained with NaHO also yielded CaO—0.0028 gram. The total CaO is thus 0.0089 gram.

41. (b.) *After reduction in a current of hydrogen.* (1.) The material, from which iron or nickel could no longer be extracted by means of the mercuric solution, was now transferred to a platinum boat and heated in a platinum tube to low redness for one hour in a current of hydrogen in which it was then allowed to cool. Its colour had now changed from reddish brown to dark grey. It was next subjected in the same way as before for two hours to the action of mercuric solution: after removal of the mercury, the colour of the residue after evaporation to dryness showed that a very considerable action had taken place.

The operation was repeated several times, and each time the extract was much too large to be negligible:—

(2) low redness for 30 minutes: mercuric solution for 2 hours.

(8)    "       "       "       "       "       all night.

(4)    "       75     "       "       "       "

(5)    "       90     "       "       "       "

(6)    "       105    "       "       "       "

(7)    "       135    "       "       "       "

As the extracts after the first were more or less the same in quantity, it seemed that the presence of the silicates was hindering the access of the hydrogen to the material to be reduced, and that only the superficial material was being affected.

(8). The whole material was next heated by seven instalments in the hydrogen current; and the mercuric solution was allowed to act for two days: there was a distinct diminution in the amount of iron which passed into solution.

(9). The material was heated by six instalments in the hydrogen and then again as a whole, while the action of the mercuric solution was continued for two days: the extracted iron was now larger than the average of those previously obtained.

(10). The material was again heated in instalments, and was twice treated with mercuric solution: it was ascertained that practically the whole of the reduced metal had been dissolved during the first treatment.

(11). The material was again heated in ten instalments and extracted twice by mercuric solution; in each case a residue was obtained which showed a negligible action, regard being had to the constant residue obtained in the later stages of the similar treatment of the attracted material.

42. During the heating in the platinum tube, the issuing gas was allowed to bubble through water which served to retain the expelled mercury and its chlorides. It was remarked that in operations 2-9, the absorbing water turned brown and afterwards gave a brownish-black precipitate: this was clearly due to the formation of sulphuretted hydrogen during the passage of the hydrogen over the heated material and to the consequent precipitation of the mercury, and it indicated a considerable alteration of the troilite (ferrous sulphide): after the ninth operation the discolouration and subsequent precipitation were no longer observed. This suggests that the protracted character of the extraction is due to the gradual alteration of the troilite. In most of the extracts as obtained after evaporation there was visible some white non-volatile powder, suggesting the presence of magnesia and therefore an action on the silicates during this operation.

43. The precipitates of mercuric sulphide were slowly ignited as before, the residue dissolved and again precipitated by sulphuretted hydrogen: the small precipitate was found to be copper sulphide, and appeared to be about the same in amount as the corresponding one obtained from the 0.2471 gram of attracted material (§19): it was not weighed: the filtrate, which would contain any iron carried down with the voluminous precipitates of mercuric sulphide, was added to the collected extracts.

44. On analysis the following numbers were obtained:—  
 $\text{SiO}_2$  — 0.0054 gram (thus confirming the suspected action on the silicates)  
 $\text{Fe}_2\text{O}_3$  — 0.5138 gram.

$(\text{Ni}, \text{Co})\text{O}$  — 0.0382 gram: after reduction in hydrogen 0.0297 gram: the calculated metal from the oxide is 0.0300 gram. This gave 0.0370 gram of potassium cobalt sulphate ( $2\text{CoSO}_4, 3\text{K}_2\text{SO}_4$ ), which corresponds to 0.0053 gram of cobalt: hence the nickel and cobalt are in the proportion of 4.7:1.

[The filtrate from the nickel which had been separated by means of repeated action of ammonium sulphide yielded at this point, on again being evaporated to dryness, as much as 0.0260 gram of  $\text{SiO}_2$ , which must be due to the action on the vessels during the separation.]

$\text{CaO}$  — 0.0135 gram (part of which must likewise be due to the vessels).  
 $\text{Mg}_2\text{P}_2\text{O}_7$  — 0.0136 gram, corresponding to  $\text{MgO}$  — 0.0049 gram.

6. *Unattracted material: mercurialised residue (or part undissolved by mercuric solution).*

45. In such a series of operations as has just been described, it was clear that it was impossible to obtain with any approach to accuracy the

whole of the material which had been left unacted upon by the mercuric solution: accordingly the part adhering to the filter was not ignited and weighed. After the above removal of the mercury and its chlorides from the available residue, it was found that there remained 4.6037 grams of mercurialised material for examination.

46. (a.) *Sulphur and phosphorus.* Proceeding in the same way as before, it was found that 0.7671 gram of the mercurialised residue yielded only 0.0013 gram of barium sulphate and only a trace of phospho-molybdate: the iron and nickel of nearly the whole of the troilite and schreibersite have thus passed into the mercuric solution.

47. (b.) *Alkalies.* These were determined as mentioned later (§71).

48. (c.) *Treatment with hydrochloric acid.* (a.) 2.5718 grams of the mercurialised residue were treated with hydrochloric acid of specific gravity 1.06 for two hours on the water bath, water being occasionally added to replace that lost by evaporation. It was then diluted with boiling water and allowed to settle, after which the supernatant liquid was decanted off. This treatment was repeated twice. On the occasion of the third treatment, the insoluble material was washed by decantation several times.

49. The extracts which contain suspended silica were filtered after settling during the night: they filtered with extreme slowness, however, and it would really have been advantageous to have evaporated to dryness before the filtration. This had been avoided because of the probable action of the acid, during evaporation to dryness, on the small amount of the finely divided enstatitic silicate which may possibly be present in a state of suspension.

50. On evaporation of the filtered solution to dryness, a small amount of silica was obtained. The other silica, still moist and admixed with the material which had not been decomposed by the hydrochloric acid, was extracted therefrom by boiling with a strong solution of sodium carbonate containing some caustic soda: after dilution with hot water and filtration on a weighed filter, the solvent operation was repeated on the residue. The practical difficulty was that at the end of the washing, which required to be as complete as possible, the insoluble finely divided residue began to pass through the pores of the filter: the residue was accordingly now transferred as far as possible to a platinum dish; that part of the material which could not be removed from the filter by washing was weighed both before ignition (0.0826 gram) and afterwards (0.0817 gram).

51. The contents of the dish were boiled with distilled water and allowed to stand all night. As the supernatant liquid was slightly opalescent, and



remained so after filtration, the liquid was decanted off and the residual material transferred to a small platinum dish, dried and weighed; this part was 1.0292 gram.

52. The decanted slightly opalescent liquid was evaporated to dryness after acidification. As the dark brown colour indicated that the residue consisted chiefly of undissolved silicate, the latter was boiled with the sodium carbonate and caustic soda mixture, which extracted only a trace, if any, of silica: this was added to the main silica and the filtrate was added to the main solution: the weight of the residual material after ignition was 0.0121 gram. The total silica obtained was 0.5982 gram.

53. ( $\beta$ .) The iron, calcium and magnesium which had passed into the sodium carbonate and caustic soda solution were likewise determined: the weights found being:—

$\text{Fe}_2\text{O}_3$ —0.0083 gram,  $\text{CaO}$ —0.0029 gram,  $\text{Mg}_2\text{P}_2\text{O}_7$ —0.0031 gram.

The corresponding bases may have passed into the solution either owing to the imperfect washing of the mixed silica and undecomposed silicate or (which is more probable) to the action of the boiling caustic soda and sodium carbonate on the latter.

54. ( $\gamma$ .) The bases present in the hydrochloric acid extract were determined by the usual methods. As it was desired for the sake of comparison with results obtained in a direct examination to weigh the alkalies present at the end of the analysis, the iron and aluminium were precipitated by ammonium acetate, the precipitation in dilute solution being repeated and then followed by cautious precipitation with ammonia.

55. After solution of the iron and aluminium precipitate in hydrochloric acid, the separation of the iron from the aluminium was effected by the caustic soda method: the solution of the bases being poured into strong solution of caustic soda and boiled for some minutes. This method, though simpler than the Deville-Cooke method used later, does not appear to be entirely satisfactory, when the proportion of the alumina is so small as is here the case: the alumina thus obtained is not completely free from iron.

56. The manganese was separated and weighed as sulphide, and a small quantity of nickel was isolated. After removal of the calcium by a double precipitation with ammonium oxalate, the magnesium was precipitated, after a preliminary expulsion of the ammonium salts, by ammonia and ammonium carbonate.

57. During the analysis the first filtrates, which should contain practically the whole of the alkalies originally present in the decomposed material, were kept apart from the remaining filtrates and washings, any alkalies

found in which must virtually be wholly due to the action of the liquids on the vessels : as it seemed likely that the alkalies may be at least partially present in solution as sulphates, they were weighed as first obtained, then converted completely into sulphates and again weighed ; they were afterwards separated by Finkener's method, *i.e.* precipitated together by means of platinum chloride, rinsed, then washed with a mixture consisting of two parts of alcohol and one of ether ; the sodium sulphate removed by washing with ammonium chloride solution ; the residual  $K_2PtCl_6$  decomposed by heating in a current of hydrogen at a temperature of  $246^\circ C.$ , and the potassium chloride extracted with water.

58. The following numbers were obtained :—

$Fe_2O_3$	...	...	0.3532 gram	} 0.3540 gram
{ $Fe_2O_3$	...	...	0.0008	
{ $Al_2O_3$	...	...	0.0024	
$MnS$	...	...	0.0052	
$NiO$ ( $CoO$ )	...	...	0.0005	..
$CaO$	...	...	0.0078	..
$MgO$	...	...	0.5089	..

59. Alkalies from first filtrates : mixed salts before and after treatment with sulphuric acid, 0.0155 gram and 0.0159 gram respectively ; potassium chloride 0.0013 gram.

60. Alkalies from subsequent filtrates : mixed salts before and after treatment with sulphuric acid, 0.0047 gram and 0.0047 gram respectively ; potassium chloride 0.0009 gram.

61. An indirect but more satisfactory determination of the alkalies in the part extracted by hydrochloric acid is given later (§ 86) : it is finally inferred that even the alkalies of the first filtrates are wholly due to action of the liquids upon the glass or porcelain vessels.

7. *Unattracted material : the residue after treatment with mercuric solution and hydrochloric acid.*

62. (a.) The alkalies were determined by direct extraction (see § 72).

63. (b.) 0.5115 gram was fused with a mixture of potassium and sodium carbonates : the silica was isolated and the residual insoluble material (chromite) was weighed : the iron and aluminium having been precipitated together by sodium acetate twice and then cautiously by ammonia, and weighed together, the mixed oxides were treated by the Deville-Cooke method—that is, first heated in a platinum boat in a platinum tube in a current of hydrogen for half-an-hour by means of a Bunsen flame, and then for ten minutes in a current of dry hydrochloric acid

by means of a table-blowpipe—the operation being repeated until the iron had been completely removed and the boat and contents had attained to a constant weight: the alumina and silica were then separated by fusion with sodium bisulphate. This method has the advantage of showing by the colour of the residue whether any of the chromite has been decomposed by fusion with the alkaline carbonates. In this instance, when the operation no longer produced any change of weight, the residue was white and contained no chromium: but during the earlier stages the residue had a green tinge, and doubtless some chromium was then present and was expelled with the iron (§ 72): this was owing to the incomplete pulverisation of the mixed oxides: for, to prevent the introduction of silica during pulverisation in an agate mortar, the mixed oxides had been merely crushed in a steel mortar: this imperfectness of pulverisation made it necessary to heat no fewer than fourteen times in the hydrogen and hydrochloric acid before the iron was completely expelled: under such circumstances the chromium is likewise carried away.

64. The following numbers were obtained:—

Chromite	...	...	0·0023 gram
SiO <sub>2</sub>	...	...	0·2769 "
Fe <sub>2</sub> O <sub>3</sub> (Cr <sub>2</sub> O <sub>3</sub> )	...	...	0·0943 "
Al <sub>2</sub> O <sub>3</sub>	...	...	0·0011 "
MnS	...	...	0·0025 "
CaO	...	...	0·0203 "
{ MgO	...	...	0·0004 "
{ Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	...	...	0·3241 "

#### 8. Alkalies.

65. Various determinations of the alkalies in the unattracted material and its products were made by the method of ignition with calcium carbonate and ammonium chloride.

Proceeding in the way described by the late Professor Lawrence Smith (except that the last portion of the lime was removed by means of ammonium oxalate) 0·5851 gram of the unattracted material yielded 0·0130 gram of the mixed sodium and potassium salts, and these, when treated as if they were wholly chlorides, in turn gave 0·0028 gram of K<sub>2</sub>PtCl<sub>6</sub> besides 0·0014 gram of platinum.

66. Examination with the spectroscope showed that lithium was present.

67. As the percentage of alkalies in the unattracted material is therefore small, and it seemed likely that the mixed alkaline salts were partly

sulphates and partly chlorides, (1) a re-determination of the alkalies in the unattracted material was made, the alkaline salts being weighed both before and after evaporation with sulphuric acid: the amounts of the alkalies were also determined (2) in the mercurialised residue, (3) in the residue undissolved by the hydrochloric acid, and (4) in the material which had been treated with water, alcohol and ether. To secure uniformity both of treatment and reagents, all the weighed quantities were severally mixed with appropriate quantities of calcium carbonate and ammonium chloride before the first ignition was begun: further, a mixture of the same amount of calcium carbonate (4 grams) and ammonium chloride (0.5 gram) was prepared for a blank experiment.

68. The ignitions and extractions having been performed in immediate succession in the same way with the same reagents, it was seen that the blank experiment yielded a very appreciable quantity of alkaline salt: this extract (in the form in which it presented itself after the expulsion of the ammonium oxalate and other salts and before treatment with hydrochloric acid) weighed 0.0040 gram, and on examination was found to be essentially sodium carbonate. This alkali was traced to the calcium carbonate itself, and as that reagent had been already mixed with the various residues it became necessary to carefully determine the amount of alkalies yielded by a blank experiment.

69. The stock of calcium carbonate in use being now nearly exhausted, two blank experiments were made, in each of which only 3 grams of calcium carbonate and 0.375 gram of ammonium chloride were used.

(a). The first yielded:—mixed alkaline salts, before and after evaporation with sulphuric acid, 0.0040 gram and 0.0041 gram respectively, potassium chloride 0.0005 gram.

(β). The second yielded:—mixed alkaline salts, before and after evaporation with sulphuric acid, 0.0040 gram and 0.0045 gram respectively, potassium chloride 0.0006 gram.

For 4 grams of the calcium carbonate and 0.5 gram of the ammonium chloride the mean result is:—mixed alkaline salts, before and after evaporation with the sulphuric acid, 0.0053 gram and 0.0057 gram respectively, potassium chloride 0.0007 gram.

70. (1.) 0.4965 gram of the unattracted material gave:—mixed alkaline salts, before and after evaporation with sulphuric acid, 0.0125 gram and 0.0139 gram respectively, potassium chloride 0.0016 gram.

71. (2.) 0.5001 gram of the mercurialised residue gave:—mixed alkaline salts, before and after evaporation with sulphuric acid, 0.0095 gram and 0.0123 gram respectively, potassium chloride 0.0014 gram.

72. (8.) 0.5014 gram of the residue undissolved by hydrochloric acid gave:—mixed alkaline salts, before and after evaporation with sulphuric acid, 0.0164 gram and 0.0202 gram respectively, potassium chloride 0.0019 gram.

In this experiment, the alkaline extract as at first obtained contained some chromate clearly due to the decomposition of chromite: after reduction by evaporation with alcohol and hydrochloric acid, and precipitation with ammonia, the  $\text{Cr}_2\text{O}_3$  was determined to weigh 0.0009 gram.

A safeguard analysis of the residue freed from alkalies was likewise made, and in the course of this 0.0019 gram of  $\text{Cr}_2\text{O}_3$  was further obtained; the chromium being separated from the aluminium by chlorination of the solution of the mixed oxides in caustic soda, after expulsion of the iron by the Deville-Cooke method. The amount of chromite corresponding to the total 0.0028 gram of  $\text{Cr}_2\text{O}_3$  is 0.0041 gram: and for 0.5115 gram of the material, 0.0042 gram.

After fusion with alkaline carbonates, 0.5115 gram of the material yielded only 0.0023 gram of undecomposed chromite (§64): the two results are compatible with the inferences already made (§63), namely, that part of the chromite (0.0019 gram) was decomposed during the fusion with the alkaline carbonates, and that the chromium of the decomposed portion, after precipitation with the iron and aluminium, was slowly expelled during the separation of the alumina from the ferric oxide: even when the silicates of a residue containing chromite are decomposed by hydrofluoric acid, the passage of chromium into solution has to be looked for.

73. (4.) 0.5000 gram of the residue left undissolved by the water, alcohol, and ether, gave:—mixed alkaline salts, before and after evaporation with sulphuric acid, 0.0172 gram and 0.0179 gram respectively, potassium chloride 0.0022 gram.

### PART III.—INTERPRETATION OF THE ANALYTICAL RESULTS.

74. *Atomic Weights.* The atomic weights used in the following calculations are those adopted by Muir and Morley (1888) in their third edition of Watts' Dictionary of Chemistry, namely:—

Al	27.02	Cu	63.2	Na	23
Ba	136.8	Fe	55.9	Ni	58.6
Ca	39.9	H	1	O	15.96
Cl	35.37	K	39.04	P	30.96
Co	59	Mg	24	Pt	194.8
Cr	52.4	Mn	55	S	31.98.

It is convenient to make the calculations in the following order.

1. *Residue undissolved by hydrochloric acid.*A. *After being boiled with sodium carbonate and caustic soda.*

75. *Alkalies.* After allowing for 0.0057 gram of mixed sulphates and 0.0007 gram of potassium chloride as deduced from the blank experiments (§69), it is seen that 0.5014 gram of residue (§72) yielded 0.0145 gram of mixed sulphates and 0.0012 gram of potassium chloride: these correspond to  $K_2SO_4$  — 0.0014 gram,  $Na_2SO_4$  — 0.0181 gram, and to  $K_2O$  — 0.000757 gram,  $Na_2O$  — 0.00572 gram. Hence for 0.5115 gram of residue, the numbers are  $K_2O$  — 0.0008 gram,  $Na_2O$  — 0.0058 gram. It must be remembered that the residue has been boiled with strong soda solution (§50), and that the completeness of the removal of adherent soda is necessarily uncertain.

76. ( $Fe_2O_3$ ,  $Cr_2O_3$ ) — 0.0948 gram (§64). Since 0.0019 gram of chromite has passed into solution (§72), the corresponding 0.0018 gram of  $Cr_2O_3$  will be contained in the 0.0948 gram of mixed oxides, and the  $Fe_2O_3$  itself will be 0.0930 gram: further, 0.0007 gram of this corresponds to the iron of the decomposed chromite: hence the  $Fe_2O_3$  corresponding to the silicate is 0.0923 gram, and is equivalent to  $FeO$  — 0.0831 gram. The higher proportion of chromite agrees very satisfactorily with the direct determination of the amount of chromite left undecomposed by hydrofluoric and sulphuric acids (§§89, 109).

$Mg_3P_2O_7$  — 0.3241 gram (§64) corresponds to  $MgO$  — 0.1169 gram.

$MnS$  — 0.0025 „ (§64) „ „  $MnO$  — 0.0020 „

77. Hence (§64) we deduce for the residue undissolved by hydrochloric acid:—

Chromite	...	...	0.0642 gram	} silicate 0.5078 gram
$SiO_2$	...	...	0.2769 „	
$Al_2O_3$	...	...	0.0011 „	
$FeO$	...	...	0.0881 „	
$MnO$	...	...	0.0020 „	
$MgO$	..	...	0.1173 „	
$CaO$	...	...	0.0208 „	
$Na_2O$	...	...	0.0058 „	
$K_2O$	...	...	0.0008 „	

---

Total 0.5115 gram

---

Taken 0.5115 „

78. The silicate has thus the following percentage composition :—

				Oxygen.
SiO <sub>2</sub>	...	...	54.58	28.98
Al <sub>2</sub> O <sub>3</sub>	...	...	0.22	0.10
FeO	...	...	16.88	8.64
MnO	...	...	0.40	0.09
MgO	...	...	23.12	9.24
CaO	...	...	4.00	1.14
Na <sub>2</sub> O	...	...	1.14	0.29
K <sub>2</sub> O	...	...	0.16	0.03
			100.00	14.58

79. This is the composition after the material has been boiled with the soda mixture; it corresponds very closely to a silicate having the enstatitic formula  $R''O.SiO_2$ : it is clear that three extractions with hydrochloric acid (§48) are at least sufficient for the complete removal of the olivinic silicate.

80. *Weight of total residue undissolved by the hydrochloric acid.*

(a). Weight of residue in dish 1.0292 gram (§ 51).

(β). Weights of ignited residues 0.0121 gram and 0.0817 gram respectively (§§ 52, 50), or together 0.0938 gram: according to the last paragraph these correspond to 0.0921 gram of unignited residue.

The total residue before ignition would thus be 1.1213 gram, consisting of 0.0092 gram of chromite and 1.1121 gram of silicate having the percentage composition given in § 78.

B. *Before being boiled with sodium carbonate and caustic soda.*

81. To find the composition of the undissolved silicate before the action of the solution by means of which the liberated silica was extracted, it is necessary to take account of the bases found in the sodium carbonate and caustic soda solution (§ 53): the amounts found correspond to the action of that solution upon an amount which yielded 1.1121 gram of undissolved silicate (§80), if we assume that the bases are due to such action, and not to the adherence to the undissolved silicate of the solution containing the bases of the silicate dissolved by the acid.

The bases corresponding to  $Mg_2P_2O_7$  — 0.0081 gram,  $Fe_2O_3$  — 0.0088 gram are MgO — 0.0012 gram, FeO — 0.0079 gram: the weight of CaO was determined to be 0.0029 gram.

82. If these correspond to silicates of the above type  $R''O.SiO_2$  we have:—

MgO	FeO	CaO	Total
0.0012 gram	0.0079 gram	0.0029 gram	0.0120 gram
SiO <sub>2</sub> 0.0018 „	0.0066 „	0.0031 „	0.0115 „
		Silicate	0.0235 „

The above silica 0.0115 gram, due to the action of the sodium carbonate and caustic soda on the enstatitic residue, will have passed into the main silica resulting from the decomposition of the other silicate by the hydrochloric acid and must be deducted therefrom.

83. As only 0.5073 gram of the undissolved silicate (§77), not the whole 1.1121 gram (§80), was used for analysis, the corresponding bases and silica to be added will be:—

MgO	...	...	0.0006 gram
FeO	...	...	0.0036 „
CaO	...	...	0.0013 „
SiO <sub>2</sub>	...	...	0.0052 „

84. Hence the composition of the undecomposed silicate, before the action of the sodium carbonate and caustic soda solution, will be given by the following (§§66, 77, 83).

			Total	Percentages	Oxygen
SiO <sub>2</sub>	0.2769	+0.0052	0.2821	54.46	28.87
MgO	0.1173	+0.0006	0.1179	22.76	9.09
FeO	0.0831	+0.0036	0.0867	16.74	3.72
CaO	0.0203	+0.0013	0.0216	4.17	1.19
MnO	0.0020		0.0020	0.39	0.09
Al <sub>2</sub> O <sub>3</sub>	0.0011		0.0011	0.21	0.10
K <sub>2</sub> O	0.0008		0.0008	0.15	0.03
Na <sub>2</sub> O	0.0058		0.0058	1.12	0.29
Li <sub>2</sub> O	trace		trace	trace	
	<u>0.5073</u>	<u>0.0107</u>	<u>0.5180</u>	<u>100.00</u>	

85. C. For the total undissolved by the hydrochloric acid, we have (§§80, 82):—

Chromite	...	...	...	0.0092 gram
Silicate	{ undissolved by Na <sub>2</sub> CO <sub>3</sub> , NaHO			1.1121 gram
undissolved by HCl	dissolved	„	„	0.0235 gram
			Total	<u>1.1448 gram</u>



2. *Unattracted material: mercurialised residue.*A. *Alkalies.*

86. (a.) After allowing for 0.0057 gram of mixed sulphates and 0.0007 gram of potassium chloride, as deduced from the blank experiments, it is seen that 0.5001 gram (§71) of the mercurialised residue (before being acted upon with hydrochloric acid) yielded 0.0066 gram of mixed sulphates and 0.0007 gram of potassium chloride: corresponding to  $K_2SO_4$  — 0.0008 gram,  $Na_2SO_4$  — 0.0058 gram, and to  $K_2O$  — 0.0004 gram,  $Na_2O$  — 0.0025 gram: hence 2.5748 grams of this residue contain  $K_2O$  — 0.0021 gram,  $Na_2O$  — 0.0128 gram.

(b.) 2.5748 grams of this residue (§48) are found to yield 1.1213 gram (§80) undissolved by HCl: further, the 1.1213 grams contain  $K_2O$  0.0018 gram and  $Na_2O$  — 0.0127 gram (§78). Hence, practically, the whole of the alkalies in the mercurialised residue belong to the part which is not dissolved by the hydrochloric acid: the alkalies found in the HCl solution (§§ 59, 60) after the removal of the other bases are thus derived from the action on the vessels, and must be neglected (§122).

B. *Mercurialised residue: troilite and schreibersite.*

87. The 0.0013 gram of  $BaSO_4$  obtained from 0.7671 gram of mercurialised residue (§46) correspond to S 0.000178; hence 2.5748 grams of the residue will contain S — 0.0006 gram, which, if still present as FeS, is combined with 0.0012 gram of Fe (corresponding to 0.0015 gram of FeO) to form 0.0018 gram of FeS (troilite): 1 gram of the residue contains S — 0.00023 gram, corresponding to Fe — 0.00041 gram; the latter corresponds to  $Fe_2O_3$  — 0.00059 gram.

The schreibersite present is only a trace.

Hence almost the whole of the troilite and schreibersite was removed during the repeated reduction in hydrogen and the treatment with mercuric solution (§42).

88. C. 2.5748 grams of the mercurialised residue (§48) were acted upon with hydrochloric acid, and the liberated silica was extracted from the residue by means of sodium carbonate and caustic soda; since 0.0052 gram of MnS corresponds to 0.0042 gram of MnO, and 0.3540 gram of  $Fe_2O_3$  to 0.3186 gram of FeO, we have the following (neglecting the alkalies as explained above):

SiO <sub>2</sub>	...	...	0.5932 gram	(§52)
MgO	...	...	0.5089	} (§58)
FeO	...	...	0.3186	
CaO	...	...	0.0078	
MnO	...	...	0.0042	
Al <sub>2</sub> O <sub>3</sub>	...	...	0.0024	
NiO (CoO)	...	...	0.0005	} (§87)
S	...	...	0.0006	

89. D. As already shown (§82), 0·0115 gram of the silica belong to the enstatite brought into solution by the sodium carbonate and caustic soda; further, from the 0·8186 gram of FeO must be deducted 0·0015 gram of FeO, which contains the 0·0012 gram of Fe required to combine with 0·0006 gram of S to form troilite (§87); also the nickel (cobalt) oxide is not present as such, but either as metallic nickel (cobalt) (0·0004 gram of metal), which has escaped the mercuric solution, or as schreibersite, more probably the former.

Hence, for the silicate decomposed by the HCl, we have:—

			Percentages.	Oxygen.	
SiO <sub>2</sub>	...	0·5817	40·90	21·68	
MgO	...	0·5089	35·78	14·29	
FeO	...	0·3171	22·30	4·95	} 19·55
CaO	...	0·0078	0·55	0·16	
MnO	...	0·0042	0·30	0·07	
Al <sub>2</sub> O <sub>3</sub>	...	0·0024	0·17	0·08	
		<u>1·4221</u>	<u>100·00</u>		

90. This corresponds very approximately to a silicate of the olivinic type (R'O)<sub>2</sub>SiO<sub>2</sub>.

It must be remembered that the silicate has been repeatedly heated to low redness in hydrogen and afterwards treated with mercuric solution, and may thus have undergone some alteration (§42): further, that the hydrochloric extract will contain besides the olivinic silicate the "glass and substance resembling glass" mentioned by Professor Ulrich, and some dissolved enstatite.<sup>1</sup>

91. E. The following is the result of the analysis of 2·5748 grams of the mercurialised residue:—

Dissolved by HCl.....	{ Silicate	...	...	...	1·4221	(§89)
	{ Troilite	...	...	...	0·0018	(§87)
	{ Nickel (Cobalt)	...	...	...	0·0004	(§89)
Not dissolved by HCl	{ Chromite	...	...	...	0·0092	} (§85)
	{ Insoluble in Na <sub>2</sub> CO <sub>3</sub> , NaHO...	...	...	...	1·1121	
	{ Soluble   ,,   ,,   ,,	...	...	...	0·0235	
	Total	...	...	...	<u>2·5691</u>	
	Taken	...	...	...	<u>2·5748</u>	(§48)

3. *Unattracted material: before action of mercuric solution.*

92. *Troilite.* 1·0693 gram of the unattracted material (§86) gave

0.1780 gram of  $\text{BaSO}_4$ , corresponding to 2.2293 per cent. of sulphur, combined with 8.8986 per cent. of iron to form 6.1261 per cent. of troilite; hence, 5.6880 grams will contain 0.84845 gram of troilite, consisting of S—0.12680 gram and Fe—0.22165 gram (corresponding to  $\text{Fe}_2\text{O}_3$ —0.8166 gram).

93. *Schreibersite*. 1.0693 gram of the unattracted material (§37) gave 0.0038 gram of  $\text{Mg}_2\text{P}_2\text{O}_7$ ; taking the schreibersite to have the composition  $\text{Fe}_3\text{NiP}_4$ , this corresponds to 0.09951 per cent. of phosphorus combined with 0.35934 per cent. of iron and 0.18835 per cent. of nickel, forming 0.6472 per cent. of schreibersite: 0.35934 gram of Fe corresponds to  $\text{Fe}_2\text{O}_3$ —0.51324 gram. Hence, 5.6880 grams of unattracted material will contain 0.0368 gram of schreibersite consisting of P—0.0057 gram, Fe—0.0204 gram (corresponding to  $\text{Fe}_2\text{O}_3$ —0.0292 gram), and Ni—0.0107 gram.

4. *Unattracted material: portion dissolved by the mercuric solution, before and after reduction in hydrogen.*

94. 5.6880 grams were acted upon in this series of operations (§40): the solution contains not only the unattracted metal and the metallic part due to the reduction of the rust (of which the state of oxidation is undetermined), but also the greater part of the troilite and schreibersite, for these minerals disappear almost wholly as such during the operations: further, there has been appreciable action on one or more of the silicates, probably almost wholly on the olivine, which is most easily altered.

95. *State of oxidation of the rust.*—Since only 0.0007 gram of  $\text{Fe}_2\text{O}_3$  was obtained from 5.6880 grams of the material by means of mercuric solution before the reduction (§40), and 0.5138 gram of  $\text{Fe}_2\text{O}_3$  was obtained from the same material by means of mercuric solution after the reduction (§44), it is clear that much of the iron was present in the state of rust. The composition of iron-rust is generally said to be  $(\text{Fe}_2\text{O}_3, x\text{H}_2\text{O})$ , but this will only be true in the extreme case. It had been found that there was considerable rust also in the attracted portion, as will be discussed later; the colour of this is dark grey, and not suggestive of the higher state of oxidation, while it is strongly attracted by the magnetic needle. Its characters, and, as will be later shown (§113), the numerical results, suggest that the iron-rust of the attracted portion is wholly, or almost so, of the composition  $\text{Fe}_3\text{O}_4$ : further, Professor A. Liversidge,<sup>1</sup> after examination of a large number of specimens of the rust

<sup>1</sup> *Trans. Australasian Assoc. f. Adv. of Sc.*, 1892.

of artificial iron, recently found that  $\text{Fe}_3\text{O}_4$  is almost always present, and sometimes even forms the whole. As for the nickel, it is probably not oxidised at all, and before reduction of the rust by hydrogen was largely sheltered from the mercuric solution by the enclosing iron rust.

96. During the analysis of the attracted material it was for some time thought that there was possibly an action of the mercuric solution on the rust itself; but later the slightness of the action of the mercuric solution on the unattracted material before reduction, which still contains a large proportion of admixed rust, showed that this was not the case as regards the oxide of iron, and further that the alloy itself had been completely removed by the magnet: the existence of metallic nickel in the material at that stage of the analysis is accounted for by the fact that when separated from the metallic iron by the rusting of the latter, its feebler magnetic properties would allow of its being left behind with the rust. It had been hoped that in the part of the meteoric stone which had been selected for analysis as being least altered, even the iron had escaped oxidation: doubtless on the more weathered side of the stone, where there is an evident difference of colour, the iron has been converted into the higher oxide and hydrated.

97. As some of the troilite is still left in the mercurialised residue, it becomes necessary to know the total amount of mercurialised residue before we can say how much of the iron dissolved in the mercuric solution is due to the troilite. As already indicated, this could not be directly determined, but it may be calculated as follows:—

Let  $x$  grams be the total amount of the residue: they will contain  $0\cdot00023x$  gram of S corresponding to  $0\cdot00041x$  gram of Fe,  $0\cdot00059x$  gram of  $\text{Fe}_2\text{O}_3$ , and  $0\cdot00064x$  gram of troilite (§87). The  $5\cdot6880$  grams of material contain  $0\cdot34845$  gram of troilite (§92): hence the total amount of troilite dissolved is  $0\cdot3484 - 0\cdot00064x$  gram, corresponding to  $(0\cdot3166 - 0\cdot00059x)$  gram of  $\text{Fe}_2\text{O}_3$  (§§ 87, 92).

98. The weights deduced for the ante-reduction extracts were (§40):—  
 $\text{Fe}_2\text{O}_3 - 0\cdot0007$  gram: this we may assume to have been present before mercurialisation as iron ( $0\cdot0005$  gram) in combination with nickel, and to have escaped attraction by the magnet through entanglement in the unattracted material.

$\text{NiO}(\text{CoO}) - 0\cdot0048$  gram: probably present as nickel (cobalt)  $0\cdot0038$  gram.

$\text{SiO}_2$	0·0003	$\left\{ \begin{array}{l} 0\cdot0059 \text{ gram: probably due to action on the} \\ \text{olivine during the weathering, or during the} \\ \text{treatment with mercuric solution itself: boiling} \\ \text{water would extract } 0\cdot0306 \text{ gram of sulphate} \\ \text{and chloride from this amount of material} \\ (\S 31). \end{array} \right.$
$\text{MgO}$	0·0017	
$\text{CaO}$	0·0039	

99. The weights deduced for the post-reduction extracts were (§44):—  
 $\text{Fe}_2\text{O}_3$  0·5188 gram: probably present as  $\text{Fe}_3\text{O}_4$  (rust), troilite, and schreibersite; the presence of some  $\text{Fe}_2\text{O}_3$  in the unattracted material, however, is suggested by the reddish brown colour (§17).

$\text{NiO}$  ( $\text{CoO}$ ) 0·0382 gram: probably present as nickel (cobalt) (0·0300 gram), partly set free by the rusting of the iron of the nickel-iron, and partly in combination as schreibersite.

$\text{SiO}_2$	0·0054 gram	$\left\{ \begin{array}{l} 0\cdot0238 \text{ gram: in great part probably due to} \\ \text{action on the olivine, though part of the} \\ \text{CaO is due to action on the vessels during} \\ \text{the separation of the nickel.} \end{array} \right.$
$\text{CaO}$	0·0185 "	
$\text{MgO}$	0·0049 "	

100. Since the whole of the schreibersite (0·0368 gram) has gone into solution (§§ 46, 93) it will yield 0·0292 gram of  $\text{Fe}_2\text{O}_3$  and 0·0107 gram of Ni.

Hence of the 0·5188 gram of  $\text{Fe}_2\text{O}_3$ , 0·0292 gram will be due to schreibersite and the remainder, 0·4846 gram, to troilite and rust: from the above (0·3166—0·00059  $x$ ) gram is due to troilite: hence the residue (0·1680+0·00059  $x$ ) gram will be due to rust, and this amount corresponds to (0·1624+0·00057  $x$ ) gram of  $\text{Fe}_3\text{O}_4$ .

Of the total ante-reduction and post-reduction nickel (cobalt) 0·0338 gram, 0·0107 gram is seen to be due to the 0·0368 gram of schreibersite; hence the amount present as metallic nickel (cobalt) will have been 0·0281 gram.

101. Hence we see that the 5·6880 grams subjected to the action of the mercuric solution must have consisted of:—

Olivinic bases and silica } which pass into solution }	...	...	0·0297 gram
Metallic iron	...	...	0·0005 "
Metallic nickel (cobalt)	...	...	0·0231 "
Magnetic oxide of iron	...	...	0·1624+0·00057 $x$ gram
Schreibersite	...	...	0·0368 gram
Troilite which passes into solution	...	...	0·3484—0·00064 $x$ gram
Mercurialised residue (including some troilite which does not pass into solution)	}		... .. $x$ grams

---

Total 0·6009+0·99993 $x$  gram;

---

$$\text{whence } x = \frac{5\cdot0871}{0\cdot99993} = 5\cdot0875 \text{ grams.}$$

The whole of the residue, if it could have been collected, would have thus amounted to 5·0875 grams.

102. Hence the 5·6880 grams of unattracted material will consist of the following :—

Olivinic bases and silica which pass into solution	...	0·0297 gram	0·0767 gram
Metallic iron	...	0 0005 „	0·0013 „
Metallic nickel (cobalt)	...	0·0281 „	0·0597 „
Magnetic oxide of iron	...	0·1658 „	0·4270 „
Schreibersite	...	0·0868 „	0·0951 „
Troilite which passes into solution	} ...	0·8451 „	0·8914 „
Mercurialised residue (in- cluding some troilite which did not pass into solution)	...	5·0875 grams	13·1417 grams
Total		5·6880 „	14·6929 „

The numbers in the second column are those which correspond to the whole of the unattracted material.

103. To find the composition of the olivine before the action of the mercuric solution and the repeated reduction in hydrogen, we must allow for the olivinic bases and silica which have entered into the mercuric solution: the weights actually obtained (§§98-99), namely,

SiO <sub>2</sub>	...	...	0·0057 gram
CaO	...	...	0·0174 „
MgO	...	...	0·0066 „
			0·0297 „

were brought into solution in an experiment in which 5·0875 grams was the weight of the residue, as calculated above. Hence, for the portion 2·5748 grams (§48) the corresponding amounts will be :—

SiO <sub>2</sub>	...	...	0·0029 gram
CaO	...	...	0·0088 „
MgO	...	...	0·0083 „
			0·0150 „

104. Neglecting the indeterminate FeO brought into solution by the

partial alteration of the olivine, we have for the original composition of the olivine before the mercuric action (§89)

		Total	Per- cent- ages	Oxygen	
SiO <sub>2</sub>	0.5817 gram + 0.0029 gram	0.5846 gram	40.68	21.56	
MgO	0.5089 „ + 0.0083 „	0.5122 „	35.64	14.24	
FeO	0.8171 „ „	0.8171 „	22.06	4.90	} 19.62
CaO	0.0078 „ + 0.0088 „	0.0166 „	1.16	0.33	
MnO	0.0042 „ „	0.0042 „	0.29	0.07	
Al <sub>2</sub> O <sub>3</sub>	0.0024 „ „	0.0024 „	0.17	0.08	
	<u>1.4221 gram + 0.0150 gram</u>	<u>1.4871 gram</u>	<u>100.00</u>		

105. Since 22.06 grams of FeO correspond to 24.51 grams of Fe<sub>2</sub>O<sub>3</sub>, 100 grams of olivine will increase to 102.45 grams on ignition in air.

106. The 2.5748 grams of mercurialised residue have thus been found to consist of (§91):—

Metallic nickel (cobalt)	...	...	0.0004 gram
Residual troilite	...	...	0.0018 „
Chromite	...	...	0.0092 „
Enstatite	...	...	1.1956 „
Mercurialised olivine	...	...	1.4221 „
		Total	<u>2.5691 grams</u>
		Taken	<u>2.5748 „</u>

107. Hence for the total amount 18.1417 grams of mercurialised residue corresponding to the whole of the unattracted material we should have :—

Metallic nickel (cobalt)	...	...	0.0020 gram
Residual troilite	...	...	0.0092 „
Chromite	...	...	0.0471 „
Enstatite	...	...	5.8089 grams
Mercurialised olivine	...	...	7.2745 „
			<u>18.1417 „</u>

108. The 14.6929 grams of unattracted residue will therefore consist of the following (§102):—

Metallic iron	...	...	...	0.0018 gram
Metallic nickel (cobalt)	...	...	...	0.0597 "
Magnetic oxide of iron	...	...	...	0.4270 "
Schreibersite	...	...	...	0.0951 "
Troilite (entering into solution)		...	...	0.8914 "
Olivinic bases and silica (ditto)		...	...	0.0767 "
Mercurialised residue 18.1417 grams	{	Metallic nickel	...	0.0020 "
		Troilite	...	0.0092 "
		Chromite	...	0.0471 "
		Enstatite	...	5.8089 grams
		Mercurialised olivine	7.2745 "	
				<hr/> 14.6929 "

109. Or combining corresponding terms and including the trace of copper (§48):—

Metallic iron	...	...	...	0.0018 gram
Metallic nickel (cobalt)	...	...	...	0.0617 "
Copper	...	...	...	trace
Magnetic oxide of iron	...	...	...	0.4270 "
Troilite	...	...	...	0.9006 "
Schreibersite	...	...	...	0.0951 "
Chromite	...	...	...	0.0471 "
Olivine	...	...	...	7.8512 grams
Enstatite	...	...	...	5.8089 "
				<hr/> 14.6929 "

The above amount of chromite is 0.32 per cent. of the unattracted material: the actual percentage of chromite undissolved by the HF and  $\text{H}_2\text{SO}_4$  was 0.34 per cent. or 0.29 per cent., according as we take the weight on the filter or the weight after ignition to be more correct (§39).

*Attracted material: weight 0.4791 gram.*

110. Taking 0.2471 gram of the attracted material (§18) the following numbers have been obtained:—

1. Dissolved (§§21, 22)	...	...	$\text{Fe}_2\text{O}_3$	$\text{NiO}(\text{CoO})$
A. First seven extracts by mercuric solution	0.1666 gram	0.0808 gram		
B. Next five	"	"	0.0032 "	0.0024 "
			<hr/> 0.1698 "	<hr/> 0.0832 "



Compare these with the numbers obtained for the action of the mercuric solution on the unattracted material, namely :—

		$\text{Fe}_2\text{O}_3$	$\text{NiO}(\text{CoO})$
C. Ante-reduction extracts (§40)	...	0·0007 gram	0·0048 gram
D. Post-reduction extracts (§44)	...	0·5138 „	0·0382 „

From a comparison of C and D, it is beyond doubt that much of the extracted iron was present in the unattracted material in the state of oxide, for the quantity of troilite in the unattracted material is not sufficient to account by its alteration for this large quantity (0·5138 gram) of  $\text{Fe}_2\text{O}_3$ : further, it follows from C that the mercuric solution had practically no solvent action on the oxide of iron itself. Hence it is inferred that in B the  $\text{Fe}_2\text{O}_3$  is due to the presence of iron (alloyed with nickel) which has been sheltered from the mercuric solution by the oxide, but in that case it is likely that the  $\text{NiO}(\text{CoO})$  obtained is throughout due to nickel (cobalt) in the metallic state (or in small part as schreibersite). Indeed, it is clear *a priori* that if the nickel itself is not oxidised during this initial stage of weathering, it will be finely distributed through the iron-rust and well sheltered from the action of the mercuric solution until the oxide of iron itself has been reduced and brought into solution.

111. With the above interpretation, the 0·1698 gram of  $\text{Fe}_2\text{O}_3$  was present in the attracted material as 0·1189 gram of metallic iron, and the 0·0332 gram of  $\text{NiO}(\text{CoO})$  as 0·0261 gram of metallic nickel (cobalt), forming 0·1450 gram of nickel-iron having the percentage composition iron 82, nickel (cobalt) 18.

#### 112. 2. *Bout Residue.*

This weighed 0·0705 gram, after being heated in hydrogen below 800° C. (§26).

The 0·0036 gram of  $\text{SiO}_2$  (§28), if due to olivine, would originally be combined with 0·0032 gram of  $\text{MgO}$ , 0·0020 gram of  $\text{FeO}$ , and 0·0001 gram of  $\text{CaO}$  to form 0·0089 gram of olivine (§89).

The 0·0400 gram of  $\text{Fe}_2\text{O}_3$  (§30) corresponds to 0·0360 gram of  $\text{FeO}$ : of this 0·0020 gram is due to the 0·0089 gram of olivine: so that 0·0340 gram corresponds to rust, which will weigh 0·0365 gram if the oxide be  $\text{Fe}_3\text{O}_4$ .

( $\text{Ni}$ ,  $\text{Co}$ ,  $\text{MgO}$ ) — 0·0270 gram (§30): of this 0·0032 gram is due to the 0·0089 gram of olivine, so that 0·0238 gram corresponds to metallic nickel (cobalt) 0·0187 gram.

The ignited enstatite weighs 0·0063 gram (§29), and corresponds to 0·0062 gram of unignited enstatite (§84).

113. If the iron-rust be assumed, as before, to be  $\text{Fe}_2\text{O}_3$ , we have :—

$\text{Fe}_2\text{O}_3$	...	...	0.0865 gram
Ni(Co)	...	...	0.0187 "
Olivine	...	...	0.0089 gram
Enstatite	...	...	0.0062 "

Total 0.0703 "

Actual weight 0.0705 "

The equality of the actual and calculated weights is sufficient to justify the above interpretation of the state of oxidation of the magnetically attracted rust.

114. 3. *Ignited residue* (§24).

If the 0.0703 gram of residue in the boat were ignited, it would yield

$\text{Fe}_2\text{O}_3$	...	...	0.0378 gram
NiO(CoO)	...	...	0.0238 "
Ignited olivine	...	...	0.0091 "
Ignited enstatite	...	...	0.0068 "

Total 0.0770 "

Hence, if the percentage composition before ignition of the 0.0307 gram of ignited residue which had adhered to the filter corresponded exactly to that of the residue in the boat (which would only be true approximately), the ignited residue would itself correspond to 0.0280 gram of unignited residue.

115. We then have :—

Nickel-iron dissolved (§111)	...	0.1450 gram	
Boat residue (§113)	...	0.0703 "	
Approximate weight of ignited residue } before ignition (§114)		0.0280 "	} 0.0983 gram

Total 0.2438 "

Taken 0.2471 "

116. 0.0983 gram of residue having the composition of that in the boat (§113) would consist of

$\text{Fe}_2\text{O}_3$	...	...	0.0510 gram
Ni(Co)	...	...	0.0262 "
Olivine	...	...	0.0124 "
Enstatite	...	...	0.0087 "

Total 0.0988 "

117. The 0·2471 gram of attracted material will thus consist of

0·1450 gram (§111)	{ Fe ... ..	0·1189 gram
	{ Ni(Co) ... ..	0·0261 „
	{ Ni(Co) ... ..	0·0262 „
0·0983 gram (§116)	{ Fe <sub>3</sub> O <sub>4</sub> ... ..	0·0510 „
	{ Olivine ... ..	0·0124 „
	{ Enstatite ... ..	0·0097 „
Total		0·2433 „

118. Hence, now including the trace of copper (§19), the total attracted material, 0·4791 gram, will consist of (§117):—

Metallic iron	... ..	0·2842 gram
Metallic nickel (cobalt)	... ..	0·1080 „
Metallic copper	... ..	trace
Magnetic oxide of iron	... ..	0·1004 „
Olivine	... ..	0·0244 „
Enstatite	... ..	0·0171 „
Total		0·4791 „

119. For the whole material (attracted and unattracted) we thus have (§§109, 118):—

				Percentages
Metallic iron	... ..	0·2855 gram		1·55
Metallic nickel (cobalt)	... ..	0·1647 „		1·08
Copper	... ..	trace		trace
Magnetic oxide of iron	... ..	0·5274 „		3·48
Olivine	... ..	7·3756 grams		48·61
Enstatite	... ..	5·8260 „		38·40
Troilite	... ..	0·9006 gram		5·94
Schreibersite	... ..	0·0951 „		0·63
Chromite	... ..	0·0471 „		0·81
		15·1720 grams		100·00

The differences from the preliminary numbers mentioned in Professor Ulrich's paper are due to an assumption, found later to be incorrect (§46), that only a negligible amount of the iron in the mercuric extract of the reduced unattracted material was due to alteration of the troilite.

120. The 3·48 per cent. of Fe<sub>3</sub>O<sub>4</sub> being due to the weathering of 2·52

of metallic iron, the percentage composition of the stone before weathering would be

Nickel-iron	...	...	5.20
Olivine	...	...	49.08
Enstatite	...	...	38.77
Troilite	...	...	6.00
Schreibersite	...	...	0.64
Chromite	...	...	0.31
			<hr/> 100.00 <hr/>

121. 100 parts of the silicate portion would consist of 55.87 parts of olivine and 44.18 parts of enstatite.

100 parts of the original nickel-iron would consist of 78.94 parts of iron and 21.06 parts of nickel (cobalt) (§119): the analysis of 0.1450 gram of the residual nickel-iron gave 82 of iron to 18 of nickel (cobalt) (§111).

The nickel and cobalt are in the proportion to each other of 4.7 : 1 (§44) or of 12 : 1 (§21): the former proportion was deduced from the analysis of reduced rust, the latter from analysis of the mercuric extract of the residual unruined alloy itself, which may have a different composition.

## 122. ALKALIES.

### (1). Unattracted material.

*First determination.* After deducting the 0.0062 gram of mixed chloride due to the blank 4.6803 grams of calcium carbonate (§69), the weight of the mixed chlorides due to 0.5851 gram of the unattracted material will be 0.0068 gram (§65). Further, 0.0028 gram of potassium platino-chloride and 0.0014 gram of platinum correspond respectively to 0.0009 gram and 0.0011 gram, and together to 0.0020 gram of KCl; deducting 0.0009 gram due to the blank calcium carbonate, the KCl due to the unattracted material is 0.0011 gram: whence the NaCl is 0.0057 gram and the KCl is 0.0011 gram. These correspond respectively to 0.12 per cent. of  $K_2O$  and 0.52 per cent. of  $Na_2O$ .

*Second determination.* After deducting 0.0057 gram of mixed sulphates due to 4 grams of blank calcium carbonate, the mixed sulphates due to the 0.4965 gram of the unattracted material (§70) will be 0.0082 gram: similarly, deducting 0.0007 gram of KCl due to the blank calcium carbonate, the KCl due to the unattracted material itself is 0.0009 gram. These correspond to  $K_2SO_4$  0.0011 gram and  $Na_2SO_4$  0.0071 gram: or to 0.12 per cent. of  $K_2O$  and 0.62 per cent. of  $Na_2O$ .

(2). *Mercurialised residue.*

It has been shown (§86) that in the mercurialised residue the percentages of  $K_2O$  and  $Na_2O$  are 0.08 and 0.50 respectively.

(3). *Hydrochloric acid extract.*

The weight of silicate decomposed by the acid was 1.4221 gram (§91).

(a). The KCl from the first filtrates (§59) was 0.0018 gram, corresponding to  $K_2SO_4$  0.0015 gram : the mixed sulphates weighed 0.0159 gram : hence the  $Na_2SO_4$  weighed 0.0144 gram : these correspond to 0.0008 gram of  $K_2O$  and 0.0068 gram of  $Na_2O$ , or to 0.06 per cent. of  $K_2O$  and 0.44 per cent. of  $Na_2O$ .

(b). The KCl from the later filtrates (§60) was 0.0009 gram, corresponding to 0.0011 gram of  $K_2SO_4$  : the mixed sulphates weighed 0.0047 gram : hence the  $Na_2SO_4$  weighed 0.0036 gram : these correspond to 0.0006 gram of  $K_2O$  and 0.0016 gram of  $Na_2O$ , or to 0.04 per cent. of  $K_2O$  and 0.11 per cent. of  $Na_2O$ .

The latter amounts must be due to the action on the glass and porcelain vessels : if we assume that there was an equal amount of action in the earlier part of the analysis, the percentages due to action on the silicate itself will be 0.02 per cent. of  $K_2O$  and 0.32 per cent. of  $Na_2O$ .

It has been inferred elsewhere that there were practically no alkalies extracted by the acid (§86).

(4). *Insoluble residue*

It has been already shown (§84) that in the residual silicate undissolved by hydrochloric acid the percentages of  $K_2O$  and  $Na_2O$  are 0.15 and 1.12 respectively. As the silicate was freed from admixed silica by boiling with strong soda solution, it is not unlikely that traces of the latter may have adhered to the silicate even to the end of the boiling with distilled water.

(5). *Unattracted material (after treatment with water, alcohol and ether).*

After deducting 0.0057 gram of mixed sulphates due to 4 grams of blank calcium carbonate, the mixed sulphates due to 0.5 gram of this residue (§78) will be 0.0122 gram : similarly, deducting 0.0007 gram of KCl due to the blank calcium carbonate, the KCl due to the residue itself is 0.0015 gram. These correspond to  $K_2SO_4$  0.0018 gram and  $Na_2SO_4$  0.0104 gram ; or to 0.10 per cent. of  $K_2O$  and 0.48 per cent. of  $Na_2O$ .

The above numbers are consistent in indicating that the alkali present is essentially soda, and is almost wholly if not solely present in a mineral

constituent which is only slightly attacked by water, alcohol, ether, or dilute hydrochloric acid.

*Chemical relationship to other meteoric stones.*

123. For the olivinic silicate the ratio of the oxygen in combination with the iron and manganese to that in combination with the magnesium and calcium is 1 : 2·9 (§104); in this respect the Makariwa stone resembles those of Gopalpur (1 : 2·75), Mezö-Madaras and Eichstädt (1 : 2·8), Montréjeau and Pultusk (1 : 2·9), Borkut and Chantonney (1 : 8).<sup>1</sup>

For the enstatitic silicate the corresponding ratio is 1 : 2·7 (§84): this approximates to those of Eichstädt (1 : 2·2), Manegaum, Waconda, and Tjabé (1 : 2·8), Seres (1 : 2·4), Georgia and Montréjeau (1 : 2·5), Grosnaja (1 : 2·6), Utrecht (1 : 2·7), Ski (1 : 2·8), Borkut (1 : 8).

Of the above meteoric stones that which stands nearest in this respect for both silicates is Montréjeau: other stones approximating to Makariwa in both ratios are Borkut, Eichstädt, Tjabé, Utrecht and Linn County. In the proportion of the olivine to the enstatite there is also a close similarity: in Makariwa the proportion is 56 : 44 (§120), in Montréjeau it is 54 : 46.

The proportion of nickel (18·21 per cent.) in the alloy is higher than the average (§120), and approximates to that of Middlesbrough (23 per cent.).

*Concluding Remarks.*

124. As a result of the observations made in the course of the analysis of the Makariwa stone, the following points may be emphasised:—

1. It is advisable to first effect, as far as practicable, a magnetic separation of the mineral constituents: otherwise, owing to the malleability of the nickel-iron, the powdered material may be neither sufficiently fine nor sufficiently homogeneous as a mixture. Further, without this separation, the appreciable proportion of the iron-rust may escape observation.

2. The solution of mercuric ammonium chloride, suggested by Dr. Friedheim, is very satisfactory in being without appreciable action on any other constituent than the nickel-iron, if used as directed.

3. If the attracted material be treated with acid without previous

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<sup>1</sup> *Die Chemische Natur der Meteoriten*, von C. F. Rammelsberg. Berlin, 1879.

extraction by means of mercuric solution, the composition deduced for the nickel-iron may be completely wrong owing to the solution of iron-rust.

4. After reduction of the rust in the unattracted material by heating to low redness in hydrogen, and after subsequent treatment with the mercuric solution, no troilite or schreibersite will be left in the residue if the operations are sufficiently prolonged. There is a small, but appreciable effect on the silicate portion during the operations.

5. The enstatite can be completely freed from olivine by three extractions with hydrochloric acid (S.G. 1.06) on the water-bath, probably by two.

6. The Deville-Cooke method is very advantageous for the separation of the small quantities of aluminium and chromium from the iron.

It may be added that the microscopical characters of minerals have now been so minutely investigated that, for mere determination of the mineralogical species of the constituents, the microscopic examination of a thin section of a meteorite by the petrologist is more complete and expeditious than a chemical analysis.

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