Methods for the chemical analysis of meteorites: II. The major and some minor constituents of chondrites

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Summary. Pure dry chlorine at 250 to 350° C is shown to have no action on the principal silicate and phosphate phases of meteorites, but reacts quantitatively with the sulphide and phosphide phases and with kamacite; taenite does not react if it contains more than about 20 to 25 % Ni; some rare meteoritic minerals have not yet been tested. Volatile chlorides (including $SiCl_4$) distil, and non-volatile chlorides can be leached out with water. Based on these observations, a method has been devised and applied to the analysis of a number of chondrites and to the purification of olivine and pyroxene separated by physical methods. The amount of Si present in the metal of enstatite chondrites, and the distribution of P, Ga, Ge, Ti, Cr, Mn, Ca, and Mg between oxidized and non-oxidized phases can readily be determined, and some results are presented. From the limited data so far available, Co appears to be concentrated in kamacite; gallium in the metallic phase is mainly in the taenite; germanium is strongly siderophile in the common chondrites but some is present in the silicate of the enstatite chondrites; titanium is markedly chalcophile in the enstatite chondrites, less so in the common chondrites, and the same applies to chromium; phosphorus is present as phosphide in the enstatite chondrites, but as phosphate in the hypersthene chondrites.

CHEMICAL analysis of a stony meteorite may be directed to ascertaining its bulk composition, or the compositions of its constituent minerals, or both. Most analysts seek to ascertain both, and face a variety of difficulties: in many meteorites the constituent minerals are irregularly distributed, so that a representative sample is difficult to obtain; iron is distributed between five principal minerals, kamacite, taenite, troilite, olivine, and pyroxene, and may also be present as schreibersite, chromite, magnetite, or ilmenite; magnesia is greatly in excess of lime, and iron greatly in excess of aluminium. The older analysts also had difficulty with the determination of the very small percentages of alkalis and with the determination of small amounts of Cr and Mn in presence of much Fe, but the introduction of flame photometry for the alkalis and of colorimetric methods for Cr and Mn have overcome these troubles.

Two methods are at present in general use for the normal bulk-and-principal-minerals analysis, and in this paper we present a third method that will often have advantages. In both the older methods it has been customary to aim at a representative sample by taking 10 to 15 g or rather more: this is often much too small, as may readily be seen from fig. 1, where the size of an 18-g cube of sp. gr. 3·6 (1·7 cm) is outlined on sections of a few meteorites.

It is therefore desirable first to examine as large a polished section as possible, when a simple check on uniformity will allow of a decision on the minimum size for a representative sample; if the distribution of the phases is non-uniform, it may be preferable to make an areal analysis for the component minerals on a large polished surface, and to use this to correct the chemical analyses of a small and probably non-representative sample to obtain a more reliable bulk composition. But at the best certain trace elements, such as copper, which are commonly present as major components of rare and sporadically distributed minerals, give rise to difficulties in a bulk analysis.

Magnetic separation. The earliest meteorite analyses were made by separating metallic and non-metallic phases with a magnet (Howard, 1802). This separation is unavoidably imperfect, and analysts naturally sought for cleaner separations; but after it had been established that the sulphide in chondrites (other than enstatite chondrites)[1] is almost nickel-free FeS and that the silicates contain less than 0·01 % Ni it was realized that, by accepting these results and assuming that any acid-soluble silicate (essentially olivine) adhering to the metal has the same Mg : Fe ratio as the rest of the olivine, the analyses of a metal-rich attracted portion and a metal-poor unattracted, together with a knowledge of the Mg : Fe ratio in the olivine, can be combined to give a satisfactory bulk composition for most chondrites. The method was adopted by many analysts (e.g. Prior, 1913) and is probably superior to any of the methods in which selective solution of metal or sulphide is attempted.

Leaching with metal chlorides. Wöhler, in the search for an alternative to the magnetic separation, first sought to determine the metal by measuring the hydrogen evolved during its solution in acid (Wöhler, 1855), but was apparently not satisfied with this method; after trying and rejecting solution of the metal by trituration with iodine and water[2]

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[1] Ramdohr has found small amounts of pentlandite, chalcopyrite, chalcopyrrhotine, and valleriite in a number of chondrites, and in one olivine-pigeonite chondrite (Karoonda) the sulphide is mainly pentlandite; the enstatite chondrites carry sulphides of more electropositive metals (Zn, Mn, Ca, Mg).

[2] Fletcher (1894) implies that Wöhler or his predecessors had also tried chlorine

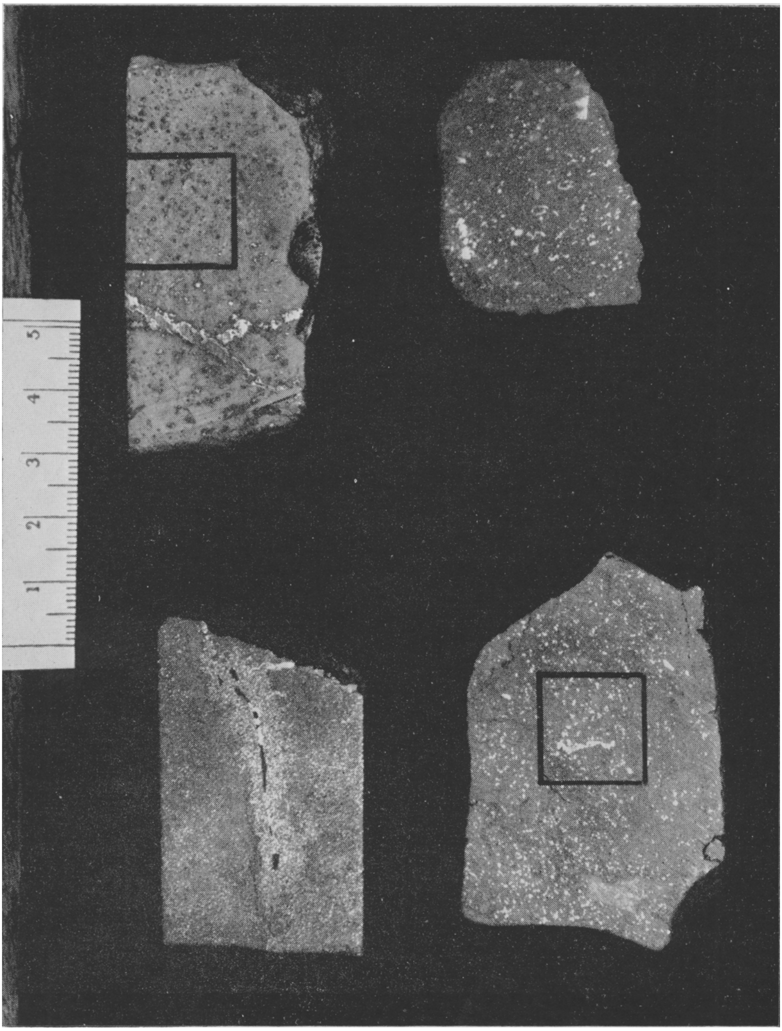

FIG. 1. Selected meteorites to show irregular distribution of metal. The lighting is arranged to show the metal reflecting. The squares outlined on two of the specimens show the side of a 1·7 cm (18 g) cube. The meteorites are: Shelburne, B.M. 1905, 435 (top left); Tadjera, B.M. 71574 (top right); Khairpur, B.M. 51366 (part) (bottom left); and Dimmitt, B.M. 1959, 856 (bottom right).

he adopted a procedure in which the metal is dissolved by aqueous cupric chloride in the cold, in completely filled flasks (Wöhler, 1863). He thought the troilite remained unattacked, but Rammelsberg (1870) showed that there is appreciable attack, not only on the troilite but to a lesser degree on the olivine. Grewingk and Schmidt (1864), indeed, thought a cupric chloride solution could give complete solution of metal and troilite without affecting the silicates. The cupric chloride method (with an addition of KCl) has recently been revived by Vilcsek and Wänke (1965).

Grewingk and Schmidt (1864) appear[1] to have been the first to use mercuric chloride solution as a solvent for the metal, though they believed it dissolved the troilite too; Rammelsberg (1866) showed that the attack on troilite is very incomplete and later (1870), after comparison with cupric chloride, he advocated digestion with mercuric chloride solution for meteorite analysis. The method has been modified by E. H. von Baumhauer (1871), C. Friedheim (1888), L. Fletcher (1894), H. B. Wiik (1956), and A. J. Easton and J. F. Lovering (1963). It is difficult to attain complete solution of the metal, and there is always appreciable attack on the troilite and on olivine.

Other liquid reagents. The chlorination procedure described below attacks both the metal (kamacite) and the troilite: in the hope of finding a reagent that would dissolve the metal without affecting the troilite, we have tried a number of reagents, but without any success: kamacite (but not nickel-rich taenite) dissolves readily in alkaline solutions of sulphosalicylic acid or ethylene-diamine-tetracetic acid when refluxed with them in a current of air—but troilite or pyrrhotine dissolves also, with liberation of sulphur; alcoholic iodine is used in steel analysis to determine oxide inclusions, and has been said to leave the sulphide undissolved, but in our tests it dissolved troilite almost as readily as kamacite; ammonium persulphate solution dissolves both kamacite and taenite readily, but the solution rapidly becomes acid (pH 1·5 to 2) through decomposition to NH_4HSO_4, and attacks both troilite and olivine markedly.[2]

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plus water and bromine plus water without success, but we have not traced any reference. Rammelsberg (1870) found that bromine plus water will dissolve both metal and troilite readily, but that the olivine is attacked. Wänke *et al.* (1965, 1966) have however, used a bromine plus water attack to remove troilite.

[1] It is difficult to be sure of the true originator—the idea of such an attack may have occurred independently to various authors. But it is clear that Rammelsberg was not led to its use for meteorites by Boussingault's work on artificial iron (1868).

[2] Begemann, Vilcsek, and Wänke (1966) have used ammonium persulphate to

Reaction with chlorine gas: preliminary experiments. Because too little material was available for a magnetic separation, Hey (1932*b*) employed a procedure for the analysis of the Suwahib (Buwah) meteorite in which dry chlorine was passed over the meteorite powder at 250° to 300° C; ferric chloride sublimed while nickel and cobalt remained as soluble chlorides in the boat. Preliminary experiments had shown no attack by the chlorine on olivine, and since the Hoba nickel-rich ataxite (16 % Ni) was completely attacked by chlorine (Hey, 1932*a*), it was assumed that the metal in the chondrite would also be completely attacked. More recently, we have found that this assumption is not correct:[1] while all the octahedrites and hexahedrites so far studied, and nickel-rich ataxites containing as much as 17 % Ni (e.g. Babb's Mill (Troost's iron) and Hoba) are completely attacked, neither San Cristobal (26 % Ni) nor Santa Catharina (34 % Ni) is affected by chlorine at 350° C; and after chlorination of an olivine–bronzite or olivine–hypersthene chondrite the boat residue is always found to contain a small amount of nickel-rich taenite.

Despite this complication, the chlorine attack appeared promising, and a study of the behaviour of various meteoritic minerals when heated in chlorine was made. In our first experiments (Moss, Hey, and Bothwell, 1961), in which the chlorine was purified by washing with water and drying with sulphuric acid, a very slight attack on olivine was sometimes apparent, and calcium carbonate slowly picked up chloride: when, however, calcium carbonate was used to absorb the traces of hydrogen chloride present in commercial chlorine (see below), no reaction could be detected between chlorine at 350° C and olivine, pyroxene, serpentine, feldspar, apatite, hematite, ilmenite, chromite, graphite, or calcite; none of these minerals shows any change in weight or in appearance,[2] and the ferrous iron content of those that contain iron remains unchanged. Cosmochlore, roedderite, merrihueite, sarcopside, graftonite,

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dissolve the metal phase preferentially, but it is evident from their table 1 that about a third of the troilite and at least 5 % of the olivine were dissolved too.

[1] That the metal must have remained partly unattacked is also evident from the high FeO found in the acid-soluble silicate compared with that in the pyroxene. Mason, Geochimica Acta, 1963, vol, 27, p. 1011, found olivine of composition Fa_{14} in Suwahib (Buwah), which agrees well with Fs_{11} in the pyroxene. Recalculating the analysis (Hey, 1932*b*, pp. 45 and 47) assuming the olivine is Fa_{14}, there must have been about 3·5 % iron present as unattacked metal, probably nickel-rich; the corrected norm would have 20 % metal, 24 % olivine, 30 % pyroxene; the true nickel content of Suwahib (Buwah) is probably nearer 2 %.

[2] Green, gem-quality olivine darkened slightly.

panethite, and farringtonite have not yet been studied, but it is expected that all will remain unattacked.

Kamacite, nickel-poor taenite, ferrosilicon, schreibersite, troilite, pyrite, chalcopyrite, daubréelite, pentlandite, oldhamite, niningerite, alabandine, osbornite, and copper are quantitatively attacked, while magnetite reacts according to the equation $6Fe_3O_4+3Cl_2 \rightarrow 8Fe_2O_3+2FeCl_3$; sinoite and perryite have not yet been studied, but the results obtained with certain enstatite chondrites indicate that they are attacked, probably quantitatively.

One main advantage of the chlorine treatment is that many of the chlorides produced are volatile: $FeCl_3$, $GaCl_3$, $GeCl_4$, $SiCl_4$, $TiCl_4$, PCl_5, and SCl_2 distil and can be recovered quantitatively from the distillates; $AsCl_3$, $SbCl_3$, VCl_4, and $SeCl_2$ may be expected to distil but this has not yet been confirmed experimentally. Direct tests have shown that, as would be expected, $CuCl_2$, $CrCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, and the alkali and alkaline earth chlorides remain with the unattacked silicates, oxides, and phosphates, from which they may be leached with water.

Experimental apparatus and methods

The *apparatus* figured[1] by Moss, Hey, and Bothwell (1961, p. 815) has been modified in the light of subsequent work: the water-filled wash-bottle immediately following the chlorine cylinder has been replaced by a tower filled with marble chips dusted with precipitated calcium carbonate (this gives a much more efficient removal of HCl); a Y-piece and a pair of taps inserted immediately before the reaction tube permits a stream of nitrogen, dried with sulphuric acid, to be passed in place of or in addition to the stream of chlorine; in the absorption train, a glass-wool plug between the empty flask and the first wash-bottle traps solid particles of ferric chloride; and the two water-filled wash-bottles have been supplemented by a third containing 40 ml of concentrated nitric acid and a fourth containing water (these have been found necessary for the complete absorption and oxidation of the distilled SCl_2).

Procedures. Direct chlorination of a meteorite powder, followed by leaching of the boat residue with water as described below, leaves an undissolved fraction consisting of all the silicates, phosphates, and oxides present in the sample, plus a small amount of nickel-rich taenite, which

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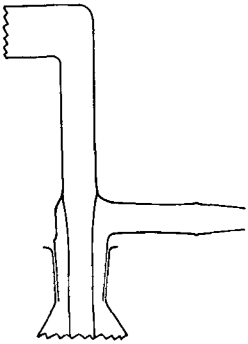
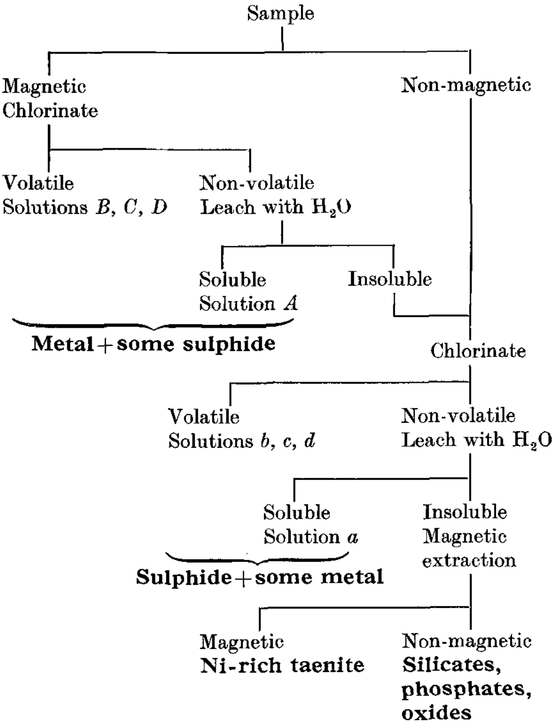
[1] There is an error in this figure: the connexion to the first wash-bottle is shown leading off from the vertical arm of the chlorination tube; in this position it would quickly become choked with ferric chloride; it should lead off so that the gas stream has first to pass through the conical flask (fig. 2).

is readily removed by a magnet; the bulk of the metal and the whole of the sulphides, phosphides, and carbides will be represented by the contents of the absorption train and the solution obtained by leaching the boat residue. For some purposes, such a set of products may be suitable, but in general we prefer to combine the chlorination with a preliminary magnetic separation: although this separation is incomplete it is sufficient to permit of a reliable calculation of the distribution of most elements between the metallic, sulphide, and oxidized phases.





FIGS. 2 and 3: FIG. 2 (left). Detail of the junction of the reaction tube and the ferric chloride receiver, to supplement and correct Min. Mag., 1961, vol. 32, p. 815, fig. 1. FIG. 3 (right). Fractionation of a meteorite sample when magnetic separation and chlorine treatment are combined.

The magnetic separation is made exactly as described by Prior (1913), the unattracted portion being reduced to pass a 100-mesh sieve before the final magnetic treatment; the size of the sample taken must be adjusted according to the coarseness of structure of the meteorite and its homogeneity, after examination of a large polished surface as well as thin sections—for a uniform, fine-grained meteorite as little as 2 to 3 g may suffice, for others a 20-g sample may still be not representative.

If a very large sample had to be taken, it may be necessary to take part only of the attracted portion for chlorination, but it is preferable to chlorinate the whole of the attracted material, for the reasons given by Prior (1913). The weighed material is placed in a porcelain boat in the reaction tube, nitrogen passed to displace the air, and the temperature raised to about 100° C with nitrogen passing, to dry the apparatus and material. The temperature is allowed to fall to 50° C before chlorine is introduced, then gradually raised to 310° C with a mixture of chlorine and nitrogen passing; after an hour, or half an hour after the distillation of ferric chloride is apparently complete, the tube is allowed to cool below 100° C, then the chlorine is discontinued and a slow current of nitrogen passed in the cold for several hours to displace chlorine from the absorption train. The porcelain boat is removed and its contents washed into a beaker, leached with water, filtered (bringing as little of the solid as possible on to the paper), and washed; the filtrates are made up to a suitable volume (50 ml for a 5-g sample of a chondrite) after addition of about 1 ml 1 : 1 HCl, and reserved (solution *A*), while the residue of silicates, etc., with possibly some nickel-rich taenite, is returned to the beaker, rinsed with a little acetone, dried under an infrared lamp, weighed, and thoroughly mixed with the unattracted portion of the meteorite.

In the dry conical flask that forms the first part of the absorption train the ferric and gallium chlorides condense, together with part of the titanium, phosphorus, and sulphur chlorides. To obtain a complete recovery of sulphur, this material must be dissolved under oxidizing conditions. Disconnect the flask, add 2 to 3 ml of bromine, stopper and stand 5 minutes, then add 5 ml concentrated nitric acid and stand a further 5 minutes; meanwhile, rinse the reaction tube and porcelain boat with 10 ml of 1 : 1 hydrochloric acid, with gentle heat if necessary to remove all iron; this solution, together with the contents of the flask, is washed into a 300 ml beaker, covered and warmed to remove bromine, then evaporated to dryness, dissolved in water with 1 to 2 ml hydrochloric acid, and made up to 100 ml (solution *B*).[1]

The contents of the first two wash-bottles are transferred to a volu-

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[1] The volumes suggested for solutions *B*, *C*, *D* refer to the attracted portion from a 5-g sample of an ordinary chondrite; for larger samples, adjust accordingly or take smaller aliquots.

metric flask (150 ml) and made up to volume with water; this solution, *C*, contains all the germanium and silicon of the attracted portion, the remainder of the phosphorus and titanium, a further part of the sulphur, and often a little iron (< 1 mg). The contents of the third wash-bottle are evaporated to dryness, dissolved in a little water and 1 ml of hydrochloric acid, the contents of the fourth wash-bottle added, and the whole made up to 100 ml (solution *D*). The determination of sulphur in solutions *B*, *C*, and *D*, and of silicon in solution *C* should be made without delay; solution *C* is apt to precipitate sulphur compounds on standing, and the silica may polymerize.

From the unattracted portion, to which the silicates, etc., from the attracted portion have been added (see above), a suitable aliquot (usually about 2 to 3 g) is taken for analysis. This is chlorinated and leached precisely as above, yielding further solutions *a*, *b*, *c*, and *d* derived from the metal, sulphide, etc., present in the unattracted material, together with a residue of silicates that will usually contain a little nickel-rich taenite, as bright, smooth particles that are readily extracted with a magnet, carrying little silicate with them; they are analysed for Fe, Ni, Co, Ge, Ga, and P by a small-scale adaptation of the methods of Moss, Hey, and Bothwell (1961), but Mg is also determined, so that a correction can be made for the iron present in adhering olivine.

After removal of this metal, the remaining mixture of silicates, phosphates, and oxides is analysed for the major constituents by standard methods,[1] except that because of the great excess of iron over aluminium the iron is preferably removed from a hydrochloric acid solution of the ammonia precipitate by *iso*-propyl ether extraction (Moss, Hey, and Bothwell, 1961) before precipitation of the remaining constituents (Al_2O_3, TiO_2, Cr_2O_3, and P_2O_5) by ammonia. Any method suited to silicate rocks may, in general, be used for the minor and trace constituents (nickel should be looked for, if only as evidence of the complete removal of metal; it has not been found in the oxidized phase of any meteorite. Thus gallium and germanium were determined in the

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[1] We have found it convenient to determine SiO_2, $Al_2O_3+TiO_2+P_2O_5+Cr_2O_3$, CaO, and MgO gravimetrically after sodium carbonate fusion; a second portion is evaporated with $HF+H_2SO_4$ and the solution used for determinations of TiO_2, P_2O_5, MnO, Cr_2O_3, total iron (as FeO), and alkalis; the small insoluble residue from the $HF+H_2SO_4$ attack is principally chromite, but should be dissolved by $K_2S_2O_7$ fusion and analysed (Mg and Al may be found as well as Cr and Fe). There is reason to suspect that many meteorites may contain small amounts of magnetite, but a satisfactory method for the determination of small quantities of Fe_2O_3 in presence of much FeO has not yet been devised; experiments in this direction are in train.

silicates of the meteorites reported on below by decomposing 0·5 g with a mixture of 10 ml hydrofluoric acid, 3 ml 1 : 1 sulphuric acid, and 0·5 ml nitric acid, evaporating twice to fumes, transferring to a distillation flask with 50 ml 1 : 1 hydrochloric acid, distilling off the germanium, and determining the gallium in the residual solution, both by the methods detailed by Moss, Hey, and Bothwell (1961).

Solutions *A*, *B*, *C*, and *D* are derived from metal plus phosphide and a minor amount of sulphide, solutions *a*, *b*, *c*, and *d* from sulphide plus a minor amount of metal and phosphide; both sets are analysed in the same way, and the results of both analyses are adjusted on the assumption that the sulphide, apart from any minor amounts of CaS, MnS, or MgS, is nickel-free FeS. The phosphide is assumed to be schreibersite, $(Fe,Ni)_3P$, with 20 % Ni, unless there is evidence to the contrary (e.g. from an electron-probe analysis).

Determinative methods for individual elements in the attacked phases. In all the procedures detailed below, solutions *a*, *b*, *c*, and *d* are treated in exactly the same way as solutions *A*, *B*, *C*, and *D* respectively, with minor exceptions, and parallel determinations must be assumed.

Sulphur. A suitable aliquot, usually a tenth (10 ml) of solution *B* is made alkaline with 2N NaOH after addition of 1 ml 30 % H_2O_2, boiled, and the precipitate filtered off, washed with a little water, and discarded (or used for an iron determination); to the filtrate are added similar aliquots of solution *C* (15 ml) and *D* (10 ml), a further 1 ml H_2O_2, and NaOH if necessary to restore alkalinity. After boiling to oxidize sulphur compounds completely and to destroy H_2O_2, the solution is acidified and sulphur determined as $BaSO_4$.

Silicon is determined by the molybdenum blue method, using 5 ml of solution *C*; it has been found only in enstatite chondrites so far, but is always present in them.

Germanium is found wholly in solution *C*; 20 ml of solution *C* are acidified with 5 ml HCl (sp. gr. 1·18), and 4 ml 10 % hydroxylamine hydrochloride added to reduce any residual chlorine; after standing 10 minutes, the remaining reagents are added (5 ml 0·5 % gum arabic and 15 ml phenylfluorone reagent) and the solution made up to 50 ml for colorimetry.

Titanium and *phosphorus* are determined on aliquots of solutions *B* and *C*. It is convenient to take 20 ml of solution *B*, evaporate to dryness, dissolve in 8N HCl and extract the iron with *iso*-propyl ether, evaporate the aqueous layer and add 30 ml of solution *C* (both being one-fifth aliquots), make up to 50 ml and take 25 ml for the determina-

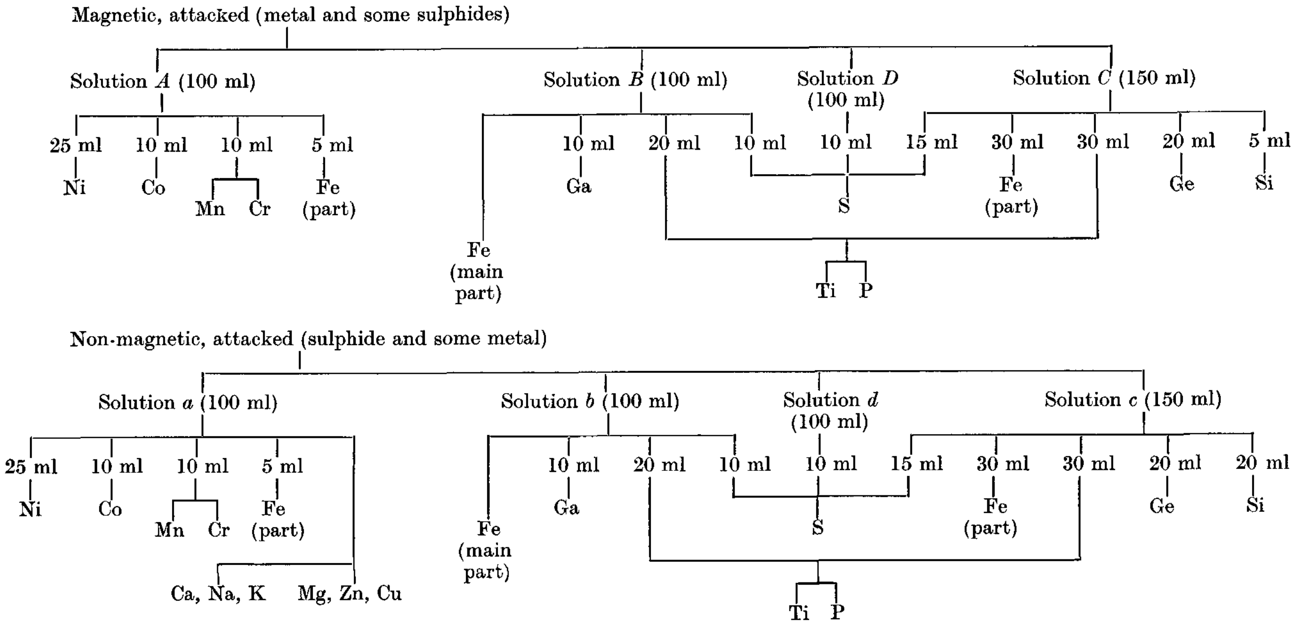

FIG. 4. Scheme of analysis for those fractions attacked by chlorine after a preliminary magnetic separation.

tion of titanium with tiron (catechol disulphonic acid) and 25 ml for phosphorus by the molybdenum blue method.

Gallium is found wholly in solution *B*, and is conveniently determined in 10 ml of this solution (but 20 ml of solution *b* should be used).

Iron is found mainly in solution *B*, but there may be a little in solution *C*, and sometimes a little in solution *A*; the small amount in solution *C* is best determined colorimetrically on a small aliquot; that in solution *B* may be determined gravimetrically, colorimetrically, or volumetrically on a suitable aliquot; that in solution *A* is best determined colorimetrically on a 5-ml aliquot, against a reagent blank to which approximately the same amount of nickel has been added as will be in the meteorite solution.

Nickel, wholly[1] present in solution *A*, may be determined gravimetrically on a 25-ml aliquot, or colorimetrically on a solution prepared by diluting solution *A* 600 times; for the unattracted fraction, solution *a* diluted 60 times will serve.

Manganese and *chromium* are determined on a 10 ml aliquot of solution *A*, after evaporation to fumes with sulphuric acid to expel chloride and oxidation with persulphate and silver nitrate catalyst; after measurement of the permanganate colour, the permanganate is reduced with 0·1 % ethylene-diamine tetracetic acid and the chromium determined with diphenyl carbazide (Easton, 1964).

Cobalt is determined on a 10 ml aliquot of solution *A*, which is diluted to 50 ml and 20 ml taken for the determination according to Moss, Hey, and Bothwell (1961); for the unattracted portion, 10 ml of solution *a* are used direct.

Sodium and *potassium* can usually be detected by flame photometry in the aqueous extract of the boat residue from the unattracted fraction of an enstatite chondrite (solution *a*); since they are not detected in the attracted fraction, nor in leachings from chlorinated albite, and since they are only found in the extract from enstatite and not from bronzite or hypersthene chondrites, we conclude that they do not originate from contamination, nor from a slight reaction between chlorine and the silicates, and that they are probably present in a sulphide phase.

Magnesium was determined in an aliquot of solution *a* by atomic absorption, and *calcium* by flame photometry. *Zinc* and *copper* were

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[1] In some of our earlier experiments traces of nickel were found in the ferric chloride flask, having been carried over mechanically by rapidly vaporizing ferric chloride; dilution of the chlorine with nitrogen and a more gradual raising of the temperature has prevented this.

not determined in the five meteorites reported on below, but may be determined in a sufficiently large aliquot, either by atomic absorption or by colorimetry.

Composition of the olivine and pyroxene. Although the Fe : Mg ratios in the olivine and in the pyroxene may be determined by the electron-probe or by physical methods (refractive index, X-ray), it is desirable to be able to determine them chemically, particularly if the minerals are zoned or variable in composition, as they are in many meteorites. A satisfactory determination may be made on the pure silicate plus phosphate fraction obtained by chlorination and leaching with water. About 0·2 g of this material is digested on the water-bath with dilute hydrochloric acid (sp. gr. 1·06); this will dissolve olivine, together with any magnesium- or iron-bearing phosphates, and will attack the pyroxene slightly, but since the amount of the phosphates will always be small and the Fe : Mg ratios in the olivine and pyroxene do not differ greatly, the resulting error will be negligible. The solution is filtered, evaporated, and silica expelled by evaporation with hydrofluoric and sulphuric acids; the residue will contain very little but the iron and magnesium of the olivine, which may be separated by an ammonia precipitation, after which the iron is determined colorimetrically and the magnesium precipitated as magnesium ammonium phosphate and weighed as the pyrophosphate.

The unattacked silicates are evaporated with hydrofluoric and sulphuric acids, and used to determine the Fe : Mg ratio in the pyroxene, using the same methods.

Although a determination of the Fe : Mg ratio in either the olivine or the pyroxene would be sufficient for the interpretation of the analysis, since the bulk Fe : Mg ratio has been determined, it is preferable to determine both, in order to have an internal check. It should be a general policy in all meteorite analyses to make as many determinations as possible in view of the irreplaceable nature of the material.

Results

If the chlorination and the magnetic removal of nickel-rich taenite (if any) have been properly carried out, the oxidized phase should contain no detectable nickel, and is reported in terms of oxides. The calculation of the Wahl norm is made in the usual way, except that instead of assuming the same Fe : Mg ratio for olivine and pyroxene the directly determined values are used.

TABLE I. Bulk percentage composition of five meteorites. *Figures in italics are parts per million.* Analyst: A. J. Easton. For notes see table II

	Barwell*	Ohuma† (H)		Wold Cottage‡	Oakley§	Khairpur‖
	(H)	1	2	(H)	(B)	(E)
Non-magnetic, attacked (sulphides):¶						
Fe	3·96	4·24	5·0	3·92	3·02	6·11
Mn	*<20*	*<20*	—	*<20*	*<20*	0·19
Ca	*<440*	*<270*	—	*<550*	*<270*	0·34
Ti	*12*	*7*	—	*8*	*19*	*720*
Cr	*1·2*	*1·7*	—	*0·7*	*1·8*	*800*
Ge	*<0·5*	*<0·5*	—	*<0·5*	*<0·5*	*<1·5*
Ga	*0·19*	*0·93*	—	*0·12*	*0·43*	*<0·5*
S	2·27	2·43	2·8	2·25	1·74	3·95
Total	6·23	6·67	7·8	6·17	4·76	10·74
Magnetic, attacked (metal and schreibersite):¶						
Fe	5·92	6·00	8·5	7·03	12·07	14·8
Ni	0·62	0·77	1·2	0·58	0·87	1·22
Co	0·05	0·05	0·1	0·048	0·065	0·02
Si	*<6*	*<4*	—	—	*<6*	0·22
Ge	*7·78*	*8·9*	—	*5·1*	*9·2*	*19·4*
Ga	*0·46*	*1·02*	—	*0·69*	*1·56*	*10·8*
P	*<15*	*<15*	—	*<15*	*<15*	0·11
Total	6·59	6·82	9·8	7·66	13·0	16·4
Magnetic, unattacked (nickel-rich taenite):						
Fe	1·03	1·03	—	1·13	3·47	—
Ni	0·64	0·50	—	0·66	0·82	—
Co	0·0044	0·005	—	0·004	0·0004	—
Ge	*2·38*	*1·8*	—	*1·89*	*1·23*	—
Ga	*0·56*	*0·55*	—	*0·73*	*1·23*	—
P	*<1*	*<1*	—	*<1*	*35*	—
Total	1·67	1·54	—	1·79	4·29	Nil
Non-magnetic, unattacked (silicates, phosphates, oxides):						
SiO_2	40·2	40·03	38·4	39·45	37·44	43·66
TiO_2	0·11	0·093	0·11	0·10	0·11	<0·006
Al_2O_3	2·48	2·41	2·7	2·37	2·26	2·42
Cr_2O_3	0·28	0·28	0·61	0·19	0·23	0·19
FeO	13·9	13·94	13·1	13·70	10·22	0·30
MgO	25·44	24·79	23·4	25·07	24·47	24·56
MnO	0·36	0·36	0·26	0·35	0·31	<0·02
CaO	1·69	1·56	1·8	1·53	1·69	0·27
Na_2O	0·99	1·02	1·1	1·00	0·88	0·90
K_2O	0·096	0·10	0·1	0·089	0·066	0·074
P_2O_5	0·17	0·17	0·07	0·21	0·27	<0·02
C	—	—	—	—	—	0·41
H_2O	0·1	0·20	0·20	0·1	0·15	0·19
Ge	*<0·4*	*<0·4*	—	*<0·4*	*<0·4*	*1·6*
Ga	*3·0*	*3·3*	—	*4·0*	*1·9*	*0·4*
Total	85·82	84·95	81·8	84·16	78·10	72·99
Grand total	100·31	99·98	99·4	99·78	100·15	100·1

TABLE II. Wahl norms and ratios for the five meteorite analyses. Italic figures are parts per million

		Barwell* (H)	Ohuma† (H) 1	Ohuma† (H) 2	Wold Cottage‡ (H)	Oakley§ (B)	Khairpur‖ (E)
Troilite		6·23	6·67	7·8	6·17	4·76	9·59
Alabandine		*<30*	*<30*	—	*<30*	*<30*	0·30
Oldhamite		*<800*	*<500*	—	*<1000*	*500*	0·60
Daubréelite		*3·4*	*4·8*	—	*2·0*	*5·0*	0·21
Schreibersite		*<100*	*<100*	—	*<100*	0·02	0·69
Metal		8·26	8·36	9·8	9·45	17·3	15·7
Graphite		—	—	—	—	—	0·4
Apatite		0·40	0·40	0·17	0·50	0·64	0·05
Ilmenite		0·21	0·18	0·21	0·18	0·20	0·01
Chromite		0·41	0·56	0·90	0·28	0·34	0·28
Feldspar		10·9	10·6	12·02	10·69	9·86	9·15
Diopside		3·9	4·1	4·96	3·54	3·64	nil
Pyroxene		25·50	26·83	20·82	23·62	25·48	62·0
Olivine		44·38	42·05	42·52	45·25	37·76	nil
Quartz		nil	nil	nil	nil	nil	0·97
% Ni in meta		15·3	15·2	12·2	13·1	8·8	6·9
Ratio Ni : Co		23	23	—	24	26	53
Ratio Mg : Si		0·943	0·923	0·908	0·947	0·973	0·838
Feldspar	An	19	18	17	15	20	14
	Or	5	5	5	5	4	5
Fa % in olivine	obs.	23·7**	23·5	23·5	24·4	18·8	—
	adj.	24·0	24·4	24·1	24·6	19·3	—
Fs % in pyroxene	obs.	19.1**	18·5	18·5	18·8	15·5	0·5
	adj.	19·2	18·9	18·7	18·9	15·6	—
Fe : (Fe+Mg+Mn)		23·0	23·5	23·3	23·1	18·6	0·5

Notes to tables I and II:

* B.M. 1966, 59. Previous analysis on the same specimen, Min. Mag., 1966, vol. 35, p. 890.

† B.M. 1966, 53. Analysis 2 made in 1965 by the magnetic separation method on another piece of the same specimen.

‡ B.M. 1073. B. Mason (Geochimica Acta, 1963, vol. 27, p. 1011) found Fa 24 % in the olivine.

§ B.M. 84814. B. Mason (*loc. cit.*) found Fa 21 % in the olivine. H. L. Preston and J. M. Davison found 14·4 % metal containing 10·8 % Ni (Amer. Journ. Sci., 1900, ser. 4, vol. 9, p. 410). K. Keil (Chemie der Erde, 1962, vol. 22, p. 281) found by planimetric analysis 14·6 % metal, 4·6 % trolite, and 0·46 % chromite. K. Keil and K. Fredriksson (Journ. Geophys. Res., 1964, vol. 69, p. 3487) found 18·3 % Fa in the olivine and 16·5 % Fs in the pyroxene. Previous analysis by H. B. Wiik in W. Wahl, Min. Mag., 1950, vol. 29, p. 419.

‖ B.M. 51366. B. Mason (Geochimica Acta, 1966, vol. 30, p. 23) found An 18 in the feldspar. Previous analysis by G. T. Prior, Min. Mag., 1916, vol. 18, p. 17.

¶ These partial analyses have been adjusted for the metal content of the sulphides and the sulphide content of the metal fraction.

** Electron-probe determinations. Keil and Fredriksson (*loc. cit.*) found, for meteorites having the same olivine compositions as the present three olivine–hypersthene chondrites, pyroxene compositions averaging Fs 20·4 %.

For the new analyses reported in table I the Fe : Mg ratio was determined in both olivine and pyroxene, and the percentages and compositions of these minerals in the norms (table II) were calculated by adjustment using a least-squares technique,[1] weighting the data on the following assessed probable errors: SiO_2 ±0·3 %, FeO ±0·35, MgO ±0·20, Fa % in olivine ±0·6, Fs in pyroxene ±0·6. Only for Ohuma were adjustments of more than half these assessed probable errors required.

The three fractions, nickel-rich taenite, metal plus some sulphide, and sulphide plus some metal, are interpreted on the following assumptions: after forming CaS, MnS, MgS, and daubréelite with any Ca, Mn, Mg, and Cr in these fractions, all remaining sulphur is reported as FeS (since we know that the nickel content of troilite is always small); all the nickel, cobalt, and silicon are referred to the metal; and any phosphide phosphorus is reported as schreibersite with an assumed Fe : Ni ratio of 3·3 unless it is known (e.g. from electron-probe analyses) that the ratio is different. These assumptions are not always justified, since we know that some of the nickel and silicon in enstatite chondrites may be present as perryite, and that some of the nickel and sulphur of common chondrites (and most of the nickel in olivine-pigeonite chondrites) may be present as pentlandite.

Five meteorites analysed by the present methods are reported on in tables I, II, and III; they comprise three olivine-hypersthene chondrites (H), one olivine-bronzite chondrite (B), and one enstatite chondrite (E). Excellent agreement with previous analyses was obtained, but the new methods yield considerable additional information.

Phosphorus in the enstatite chondrite is present mainly, if not wholly, as schreibersite, as might be expected, while in the three olivine-hypersthene chondrites it is present wholly as a phosphate mineral; in the olivine-bronzite chondrite, that part of the metal attacked by chlorine contained no phosphorus, but the nickel-rich taenite, amounting to 25 % of the total metal, contained 0·08 % phosphorus, either in solid solution or possibly as 0·5 % of included schreibersite.

In the three olivine-hypersthene chondrites, the nickel-rich taenite contained 32 to 38 % *nickel*, but the part of the metal attacked by chlorine is evidently not all kamacite, as its nickel content ranges from 7·6 % in Wold Cottage and 9·3 % in Barwell to 11·2 % in Ohuma; in the bronzite-chondrite the nickel-rich taenite contains only 19 % nickel, while the attacked metal may be wholly kamacite, as its nickel content is 6·7 %.

The distribution of *cobalt* is surprising: in the three olivine-hypersthene

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[1] W. E. Deming, Statistical Adjustment of Data (Wiley, New York), 1943, p. 59 ff.

chondrites the concentration of Co in the attacked metal is three times that in the nickel-rich taenite, while in the olivine-bronzite chondrite this ratio is about 50 (the Ni : Co ratio for total metal is around 20 to 26 for the four common chondrites and over 50 for the enstatite chondrite, in general agreement with literature data).

TABLE III. Distribution of Ga, Ge, Ti, Ni, and Fe between the several phases of the five meteorites analysed.

	Barwell (H)	Ohuma (H)	Wold Cottage (H)	Oakley (B)	Khairpur (E)
Gallium (ppm) in:					
Sulphide	3	14	2	9	0
Silicate	3·7	3·9	4·8	2·4	0·7
Ni-rich taenite	33	35	39	28	—
Attacked metal	7	15	9	12	69
Total metal	12	19	15	16	69
Germanium (ppm) in:					
Sulphide	<0·1	<0·1	<2	<8	0
Silicate	<0·5	<0·5	<0·5	<0·5	2·5
Ni-rich taenite	140	112	101	46	—
Attacked metal	118	130	66	71	123
Total metal	122	127	73	65	123
Titanium (ppm) in:					
Sulphide	192	100	132	398	7500
Silicate	780	660	720	840	<60
Cobalt (per cent) in:					
Ni-rich taenite	0·26	0·30	0·21	0·01	—
Attacked metal	0·79	0·76	0·63	0·50	0·13
Total metal	0·66	0·66	0·55	0·38	0·13
Nickel (per cent) in:					
Ni-rich taenite	38·3	32·5	36·9	19·2	—
Attacked metal	9·3	11·2	7·6	6·7	6·9
Total metal	15·2	14·8	13·1	8·8	6·9
Iron (per cent) in:					
Metal and sulphide	10·9	11·3	12·1	18·6	20·9
Oxidized phases	10·8	10·8	10·6	7·9	0·23

Titanium in the enstatite chondrite is very strongly concentrated in the 'sulphide' phase, the distribution ratio sulphide : silicate exceeding 100 (the Ti is probably present as titanoan troilite, but any that may be present as osbornite would also be attacked by chlorine and counted here). In the common chondrites it is mainly in the silicate phase, but there is still an appreciable concentration in the sulphide, the distribution ratio being about 0·5 in the olivine-bronzite chondrite and 0·2 in the olivine-hypersthene chondrites.

Previous attempts[1] to determine the distribution of *germanium* between the metallic, sulphide, and silicate phases have been hampered by incomplete removal of metal from the silicates; estimates of the distribution ratio non-magnetic : magnetic range from 0·2 to 0·005 for the few common chondrites studied. Our results suggest that the ratio is probably less than 0·005 for the common chondrites, and that the higher values are merely due to imperfect removal of metal; only in the enstatite chondrite was there appreciable germanium in the silicate: 2·5 ppm, the distribution ratio being about 0·02. Germanium was not detected in any of the sulphides. There is no marked difference between the concentration of germanium in the nickel-rich taenite and that in the attacked metal (table III).

Onishi and Sandell[2] found a very small range of *gallium* content (4·2 to 6·8 ppm, with a mean of 5·3 ppm) in 19 olivine-bronzite and olivine–hypersthene chondrites; in a composite sample, they found 3·2 ppm in the silicate, 12 ppm in the sulphide, and 15 ppm in the metal. These results are in good agreement with ours (table III), but we find a considerable variation in the gallium content of the sulphide phase in our small sample of common chondrites. The behaviour of gallium in the enstatite chondrite (Khairpur) is roughly what one would expect; the distribution ratio silicate : metal, which was about 0·2 for the common chondrites, has fallen to 0·01 in the more reduced class of meteorite. Unlike cobalt, which is concentrated in the attacked metal, and germanium, which shows no clear preference, gallium is strongly concentrated in the nickel-rich taenite.

Chromium is markedly lithophile in all the chondrites studied, but traces of daubréelite are present in all four common chondrites, and considerably more in the enstatite chondrite.

Calcium and *manganese* are still more strongly lithophile than chromium, and only in the enstatite chondrite were they found in the sulphides.

Sodium and *potassium* were not detected in the sulphide phase of Khairpur, but have been detected in this phase in certain other enstatite chondrites, and are presumably present in some as yet unidentified mineral attacked by chlorine.

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[1] S. A. El Wardani, Geochimica Acta, 1957, vol. 13, p. 5; M. Shima, *ibid.*, 1964, vol. 28, p. 517; [E. S. Burkser, K. I. Lazebnik, and K. N. Alekseeva] Е. С. Бурксер, К. И. Лазебник и К. Н. Алексеева, Метеоритика (Meteoritika), 1962, no. 22, p. 94.

[2] H. Onishi and E. B. Sandell, Geochimica Acta, 1956, vol. 9, p. 78.

Since the above results are based on a very small sample of meteorites, they may well be amended by further work, but they suggest the desirability of further analyses by the new method.

The chlorination procedure has also been applied to the purification of samples of olivine and pyroxene separated by physical methods; the results obtained will be reported elsewhere.

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Note added in proof: Since this paper went to press, a paper by L. H Fuchs (Science, 1966, vol. 153, p. 166) has come to our notice. Fuchs found small amounts of a new potassium copper iron sulphide, which he names djerfisherite, in two enstatite chondrites; our analyses show both potassium and sodium in the sulphide phase of several enstatite chondrites. No sodium-bearing sulphide has as yet been identified in these meteorites.