
The limestones of Scotland: chemical analyses and petrography — Chapter 3

Methods of analysis

A. Chemical analysis (by H. G. M. Hardie)

Preparation of sample (Kolthoff & Sandell 1950, p. 734)

The limestone was broken into small pieces and these were repeatedly mixed and quartered until a thoroughly representative sample of about 50–100 g was left. This sample was crushed to a coarse powder, a few small fragments at a time, in a diamond mortar. The coarsely crushed powder was repeatedly mixed and quartered on a sheet of glazed paper until a sample of 15–20 g was left. This sample was passed through a 100-mesh sieve and the coarse powder remaining on the sieve ground in an agate mortar until the whole sample had passed through the sieve. The fine powder thus produced was mixed very carefully on glazed paper and transferred to a stoppered weighing bottle.

Hygroscopic moisture (H₂O–)

About 2 g of the finely powdered rock were placed in a platinum crucible or weighing bottle and dried in an oven at 105°C overnight, the loss in weight representing H₂O–.

Determination of SiO₂, Fe₂O₃, Al₂O₃, TiO₂, CaO and MgO

(Lundell & Hoffman 1948, p. 183; table 92). 1 g was placed in a 250 ml beaker and moistened with water. 50 ml HCl (5:95) were added, the beaker covered and, after the initial vigorous effervescence had subsided, the whole was warmed gently until effervescence ceased. The insoluble matter was then filtered off on a 7 or 9 cm No. 40 Whatman filter paper and washed thoroughly with hot dilute HCl. The paper and its contents were then ignited in a platinum crucible to give *Insoluble Residue*. The filtrate was reserved. The residue was fused with 4.2 g anhydrous Na₂CO₃ and the melt, after cooling, was removed from the crucible, dissolved in dilute HCl and the solution added to the filtrate from the insoluble residue.

a. Silica

The combined filtrates were evaporated to dryness in a basin. When dry the basin was covered and cooled, the residue then moistened with 5–10 ml concentrated HCl. After a few minutes about 100 ml of hot water were added and the salts dissolved. The silica was then filtered off on a No. 40 paper and washed, first by decantation and then on the paper, with hot 5:95 HCl. The filtrate was again evaporated to dryness and, when dry, was usually baked for about half an hour at 110°C in an air oven. The dry mass, when cool, was moistened with concentrated HCl and, after a few minutes, 50 ml of hot water were added to dissolve the salts. If necessary, the basin was warmed on the water bath to coagulate the silica, which was filtered off on a No. 40 paper. The basin and paper were washed with hot water and the filtrate reserved.

The small residue was ignited first in a platinum crucible and then the larger one added and similarly ignited and the crucible and contents weighed. The ignition and weighing were repeated until constant weight was attained. The impure silica was then moistened with a little water, then a few drops of 1:1 H₂SO₄ and from 5–30 ml (depending on the amount of SiO₂) of hydrofluoric acid added. The crucible was then gently heated on a water-bath or sand-bath until the silica was driven off. The residue was strongly ignited for a few minutes and then weighed—the loss in weight representing silica. The residue was fused with a little Na₂CO₃, dissolved in dilute HCl and added to the main filtrate from the silica.

b. Sesquioxides

The filtrate from the silica was diluted to 300–350 ml, concentrated HCl added and then nearly neutralised with ammonia. One gramme of solid ammonium persulphate was added to oxidise manganese, and after it was dissolved the solution was made just alkaline to litmus. The solution was then heated to boiling, boiled for two minutes and ammonia added until it was again alkaline to litmus. The precipitate was filtered off immediately on a No. 41 Whatman filter paper, washed moderately with hot neutral 2 per cent solution of ammonium chloride, and the filtrate reserved. The precipitate was dissolved in 50 ml of hot dilute 1:5 HCl containing a few drops of sulphurous acid, cooled, diluted and the sesquioxides precipitated as before. The first paper was added and macerated after the precipitate was formed (i.e. just before boiling) and then the whole was filtered, washed thoroughly and the filtrate combined with the first one and retained for determination of calcium and magnesium.

The paper and precipitate were ignited in a platinum crucible, gently at first until the paper was completely charred, and finally for half hour periods over a Meker burner until constant weight was attained.

The sesquioxides were then fused with a suitable amount of potassium bisulphate (3–7 g), the melt dissolved in water containing a little sulphuric acid (2 ml, 2N) and the solution retained for the determination of iron and titanium. The crucible was washed, dried and ignited. This last weight, subtracted from that of the crucible plus sesquioxides, gave the weight of $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--TiO}_2\text{--P}_2\text{O}_5\text{--Mn}_3\text{O}_4$.

c. Aluminium

Fe_2O_3 , TiO_2 , P_2O_5 and Mn_3O_4 were determined as described below and their combined weights subtracted from the total weight of oxides obtained as above gave the weight of Al_2O_3 .

d. Iron

The solution of the bisulphate melt was kept at about 100 ml. It was passed through a Jones' reductor (Cumming & Kay 1934, p. 114) at a rate not exceeding 100 ml per minute and collected in a filter flask. After the unknown solution, 50 ml 0.2N H_2SO_4 and 100 ml distilled water were run successively through the reductor. The reduced solution was transferred to a tall beaker (500–600 ml), 50 ml of aerated distilled water being used to rinse the filter flask, and the whole stirred vigorously for two minutes to oxidise titanium. The ferrous iron was then titrated with standard KMnO_4 (0.05N). The percentage total iron as Fe_2O_3 was calculated.

e. Titanium

This was determined colorimetrically by means of the Spekker photoelectric absorptiometer, using the blue (No. 6) filters. The solution from the iron titration was reduced in bulk by evaporation and, when cold, 10 ml of concentrated H_2SO_4 and 5 ml H_2O_2 (6%) added and the whole made up to 100 ml in a graduated flask. The colour intensity was read on the absorptiometer and compared with that of standard titanium solutions treated in the same way (Cumming & Kay 1934, p. 231).

f. Calcium

The combined filtrates from the precipitation of sesquioxides may require to be reduced in volume somewhat, but for a normal limestone the solution for the calcium precipitation should not be less than 350–400 ml. To this 5 ml of concentrated HCl were added and then 50 ml of a warm solution containing 6 g of ammonium oxalate. The whole was then heated to between 70° and 80° and 1:1 ammonia added until the solution was quite alkaline. The precipitate was allowed to settle for about one hour and the supernatant liquid poured through a No. 40 Whatman filter paper. The precipitate was washed by decantation three or four times with cold 0.1% ammonium oxalate solution, retaining as much as possible of the precipitate in the beaker. The paper was then washed three or four times with the oxalate solution and the filtrate retained. The beaker with the precipitate was placed under the filter and then 50 ml hot 1:4 HCl were poured through and the paper washed eight to ten times with hot 1% HCl. The solution was diluted to 350–400 ml again, 1 g of ammonium oxalate dissolved in a few ml of water added and the whole brought to nearly boiling point. Ammonia (1:1)

was added until the solution was alkaline to re-precipitate the calcium oxalate, which was allowed to settle for two hours or more. It was filtered as before, washed two or three times by decantation with cold 0.1% ammonium oxalate solution and then eight or ten times on the paper until free from chloride. The paper and precipitate were dried in a platinum crucible and charred; then ignited for fifteen to twenty minute periods over a Meker burner until constant weight was obtained, when the calcium was weighed as CaO.

g. Magnesium

The combined filtrates from the two calcium precipitations were evaporated to low bulk and the ammonium salts removed by treating the solution with concentrated nitric acid, in the proportion 3 g nitric acid to 1 g ammonium salts, and warming until effervescence ceased. The solution was then evaporated to dryness and the residue taken up in water. About 5 ml of concentrated HCl were added and the volume adjusted according to the amount of magnesium expected (0.1 g MgO in 150 ml). The precipitant consisted of 25 g diammonium phosphate in 100 ml of water; 10 ml of the reagent were added to the cooled magnesium solution and ammonia added, stirring vigorously, until the solution was distinctly alkaline to litmus. When the precipitate was well formed, 5–10 ml of concentrated NH_4OH were added and the beaker set aside overnight. The precipitate was filtered and washed by decantation as far as possible (using No. 40 Whatman filter paper) with cold 1:20 ammonia. It was then dissolved into the beaker in which the precipitation was carried out by pouring 50 ml warm 1:10 HCl through the filter paper and washing thoroughly with hot 1% HCl. The solution was diluted as before, cooled and about 1 ml of phosphate reagent added. Ammonia was added with vigorous stirring until the solution was alkaline and when the precipitate was well formed 5 ml were added in excess. After standing at least 4 hours the precipitate was filtered off on a No. 40 paper and washed thoroughly with cold 1:20 ammonia until free from chloride. The paper was dried in a platinum crucible, charred, the carbon carefully burned off and the precipitate ignited for 20 to 30 minute periods over a Meker burner until constant weight was obtained, when the magnesium was weighed as magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$).

Sodium and Potassium

(Lawrence Smith method) (Hillebrand & Lundell 1948, p. 788). Two grammes of powdered limestone were ground in an agate mortar to an impalpable powder, $\frac{1}{2}$ g ammonium chloride added and the two thoroughly mixed by further grinding. Then nearly all of 1–2 g CaCO_3 was added in several portions and the whole thoroughly mixed in the mortar. The bottom of a Lawrence Smith platinum crucible was lined with a little of the carbonate to prevent adhesion of the mass to the crucible on ignition. The mixture was transferred to the crucible with the aid of a long narrow spatula. The remainder of the carbonate was used for rinsing the mortar and pestle and the rinsings also transferred to the crucible. The long crucible was capped and placed in an inclined position in an asbestos board provided with a hole to receive it. The part projecting through the board (about two thirds) was heated gently by a bunsen burner with a flame spreader, placed considerably below the crucible, for about 15 minutes or until the odour of ammonia was no longer perceptible (tested with HCl bottle).

(The heat should not be strong enough to cause escape of vapours of ammonium chloride). The flame spreader was replaced by an ordinary bunsen burner, or, if necessary, two, inclined so as to give a voluminous flame which strongly heated all of the crucible that projected through the board. This was heated for 40–60 minutes and cooled. The semi-fused cake was transferred to a 4-inch porcelain basin, hot water being poured into the crucible and digested until all the remaining matter could be washed out into the porcelain basin. The cake in the dish was slaked with 1 or 2 ml of water at first, then made up to about 50 ml and the whole digested on a steam-bath until thoroughly disintegrated. When the cake had disintegrated and the solution was saturated with $\text{Ca}(\text{OH})_2$ it was filtered by decantation upon a No. 40 Whatman filter paper into a 400 ml Pyrex beaker. As much as possible of the residue was kept in the dish. A further 50 ml of water were added, any lumps broken up by gentle pressure with a pestle, allowed to settle and, when the solution was saturated with $\text{Ca}(\text{OH})_2$, again decanted. The extraction was repeated three or more times and the residue washed with 50–100 ml of hot water. The solution obtained contained, in addition to the alkalis, a large amount of calcium, more or less of any sulphate that the sample may have held and possibly magnesium if much of it was originally present (e.g. in dolomitic limestone). In the latter case, to make sure of removing magnesium the solution was evaporated to approximately 100 ml, filtered, the residue washed with a saturated solution of lime-water and the filtrate treated as

follows: Calcium was removed by precipitating with ammonium carbonate solution (2 g in 25 ml water) and ammonium hydroxide at boiling temperature in a 400 ml Pyrex beaker, which was kept covered because of effervescence. The solution was filtered, the precipitate washed with hot water, then redissolved in a little more than enough HCl and the precipitation and filtration repeated. The combined filtrates were evaporated to dryness, the ammonium salts carefully driven off at a temperature short of dull redness and the residue dissolved in 25 ml of water. Sodium and potassium were determined in this solution spectrographically by the Lundegardh flame emission method (Mitchell 1936, p. 367T).

Manganese and Phosphorus

Two grammes of powdered limestone were weighed into a platinum basin and the carbonate decomposed with nitric acid. If there seemed to be an appreciable amount of carbonaceous matter the solution was evaporated and ignited. The residue was then treated with 20 ml of strong HF and 5–10 ml of concentrated nitric acid overnight. The solution was then evaporated to dryness and the residue moistened with nitric acid and evaporated two or three times to ensure the removal of the HF. The residue was finally taken up with water, a few drops of sulphurous acid added to dissolve any manganese dioxide that might have formed, then 5 ml of nitric acid added and the whole transferred to a 250-ml beaker in which it was boiled. The insoluble matter was filtered off and the beaker and paper well washed with hot water. The filtrate was then made up to 100 ml in a graduated flask.

a. Manganese

25 ml were withdrawn from the flask and placed in a 100-ml beaker, 20 ml of concentrated nitric acid and 0.3 g of potassium periodate added and the solution boiled for fully 15 minutes, to develop the colour fully. It was then cooled and made up to an appropriate volume (100–250 ml) and the colour intensity measured in the Spekker photoelectric absorptiometer (using the green filter No. 5). The values so obtained were compared with standards of known manganese content (Cumming & Kay 1934, p. 235) similarly treated, or with a curve prepared from a series of standard manganese solutions treated as above.

b. Phosphorus

The solution remaining after withdrawing the manganese aliquot was transferred to a 250–300-ml Erlenmeyer flask. Enough ammonia was added to partly precipitate the sesquioxides, which were redissolved in the minimum amount of nitric acid. Enough was then added to make the solution about 4% with respect to this acid. 30 ml of 50% ammonium nitrate solution were then added and the solution heated to 70°–75° C. and 30 ml ammonium molybdate solution (see below) containing 1.5 ml concentrated nitric acid, were added to the hot solution and the mixture well shaken. The flask was then set aside overnight. The supernatant liquid was poured through a Gooch crucible, fitted with a sheet of filter paper (No. 50 Whatman), at the filter pump and the precipitate in the flask washed twice with small quantities of 1: 10 nitric acid, 4–6 times with 2% ammonium nitrate and finally with successive small quantities of water until the total washings approximated to 500 ml and the last washings were acid free. The precipitate was sucked dry and then transferred with the filter paper to the precipitation flask in which it was dissolved in N/10 NaOH and an excess of 5–10 ml added and the whole diluted with water to 250 ml. The solution was boiled for 20 minutes and, while still hot, titrated with N/10 H₂SO₄ using phenolphthalein as indicator, 5–10 ml again being added in excess. The solution was again boiled for 15–20 minutes, allowed to cool and finally titrated accurately with N/10 NaOH till the first trace of pink (the colour fades rapidly).

1 cc N/10 NaOH = 0.00273 g P₂O₃ (Richards & Godden 1924, p. 565).

Ammonium Molybdate Solution

121 g ammonium molybdate are dissolved in 355 ml water and 60 ml (0.88 sp. gr.) ammonia are added. 489 ml concentrated nitric acid are diluted with 1149 ml water in a 2000 ml flask and the molybdate solution added. The mixture is allowed to stand for 2 days and then filtered.

Loss on Ignition and Sulphur

a. Loss on Ignition

One gramme of powdered limestone was weighed into a platinum crucible. The crucible was placed in the hole of an inclined asbestos plate and ignited over a full bunsen flame for 15 minutes, the bottom of the crucible being about 2 inches above the inner cone of the flame. After cooling and weighing the crucible was again ignited for 5-minute periods until constant weight was obtained. The loss in weight represented loss on ignition and included hygroscopic water, combined water, carbon dioxide and any other volatile matter.

b. Sulphur

The ignited mass left from above was transferred to a 250 ml beaker and covered with water. The crucible was cleansed with dilute hydrochloric acid and the solution poured into a beaker. More acid was added until decomposition was complete in the cold or on gently warming. The solution was then filtered, diluted if necessary to 150 or 200 ml containing 1–2% hydrochloric acid by volume, brought to boiling and the sulphate precipitated with a boiling solution of barium chloride in slight excess. This was set aside for 6 hours, filtered (a Gooch crucible being used), washed, dried in an air-oven at 105°C and weighed. The BaSO_4 may be filtered through a No. 42 Whatman paper, ignited and then weighed. The sulphur content is expressed as S, SO_3 or FeS_2 , depending upon the form in which it occurs.

Previous to the above method being adopted an ignition method using 2 g Na_2CO_3 and 5 g Na_2O_2 with 1 g powdered limestone was used (Cumming & Kay 1934, p. 352). The above simplified method was found to give results which agreed very well with the ignition method and was therefore used latterly for all the limestones.

Ferrous Iron

One or two grammes of limestone, depending on how much FeO was expected, were treated with 50–100 ml of 2% H_2SO_4 and brought to the boil in order to expel any H_2S . The insoluble residue was rapidly filtered off and the ferrous iron in the filtrate titrated with standard potassium permanganate.

Carbon Dioxide: (Kolthoff & Sandell 1950, p. 385)

One gramme of powdered limestone was treated with dilute (1:1) hydrochloric acid in a flask fitted with a water condenser, which was connected with an absorption train consisting of sulphuric acid, anhydrous copper sulphate, two weighed tubes containing an alkaline absorbent (e.g. Carbosorb) and a desiccant, and then through a final tube containing fused calcium chloride. Provision was made for drawing a current of CO_2 -free air through the flask and train.

Acid soluble portion of limestone

In the cases of some limestones rich in either calcium or magnesium silicate, or both, it was necessary to determine the carbonates separately. One gramme of powdered limestone was treated with 50 ml of 10% acetic acid and warmed gently to effect complete solution of the carbonates. The residue was filtered off and washed with hot water. The filtrate was evaporated to dryness, treated with 5–10 ml hydrogen peroxide to decompose any organic matter and again evaporated to dryness. The residue was taken up in dilute hydrochloric acid and filtered if necessary. 10 ml concentrated hydrochloric acid were added to the filtrate and the sesquioxides removed before determination of the calcium and magnesium as described on p. 9.

Partial analysis of limestone

Depending on the nature of the limestone (i.e. whether it contained readily decomposed silicates) one gramme of the powdered sample was treated with 2% hydrochloric acid or 10% acetic acid until effervescence ceased, warming if necessary. The insoluble residue was filtered off on a No. 40 Whatman filter paper, washed with hot water and then ignited if the percentage of insoluble material was required.

Note: If acetic acid has been used the filtrate should be taken to dryness and treated with hydrogen peroxide as described above (under acid soluble portion of limestone) and the calcium and magnesium determined as usual after

removal of the sesquioxides.

Mr. C. O. Harvey notes that many of the methods used in the chemical laboratories of the Geological Survey and Museum for the analysis of limestones differ only in detail from the methods described above by Dr. Hardie.

There are, however, some major differences, such as the use in the Macaulay Institute of the Jones' reductor method for determination of iron, of a volumetric finish for the determination of phosphorus and of a spectrographic finish for alkali determination.

In the Geological Survey laboratories iron is determined by titration with titanous sulphate, and phosphorus and alkalis are determined by gravimetric methods.

B. Spectrographic determinations (by R. L. Mitchell)

The trace elements were determined spectrographically by a semi-quantitative technique employing a cathode layer direct current arc source. The method has been fully described elsewhere (Mitchell 1948) and is briefly as follows:

About 50 mg of finely ground limestone are mixed with an equal weight of carbon powder and filled into an 8 mm deep, 0.8 mm diameter boring in a 2.8 mm thick carbon electrode. This filled electrode is the lower, cathode pole of a 9 amp, 10 mm long, direct current arc. After three minutes the sample is completely consumed and the spectrograms of the first, second and third minutes, taken on a large quartz spectrograph, are compared in a Judd Lewis Spectrum comparator with those on standard plates prepared in a like manner from CaCO_3 to which incremental amounts of the trace elements had been added. The accuracy should be around $\pm 30\text{--}50\%$ for most of the trace elements reported.

The sensitivities of the elements sought, in parts per million, are as follows:

Ag	2	Co	5	Li	1	Sr	10
B	1	Cr	2	Mo	5	Ti	10
Ba	5	Cu	1	Ni	5	V	10
Be	5	Ga	3	Pb	10	Y	20
Bi	10	Ge	10	Rb	30	Zn	1000
Cd	200	La	25	Sn	10	Zr	10

Other elements looked for on a qualitative basis, but not observed, included As, Ce, Cs, Hg, Sb, Te and W, all of which are relatively insensitive by the technique employed. The carbon electrodes available during the war years were not free from Cu and on this account results for this element are not generally available.

In the spectrographic tables a dash indicates a content below the sensitivity. A blank indicates the absence of data for the sample in question and refers chiefly to B and F for which only a few samples were examined. Other elements detailed above but not quoted were always below the sensitivity level.

The Strontium content of limestones and dolomites

In general, the contents of trace elements in limestones are low, and the higher values occur in those with large insoluble residues of an argillaceous character. An inspection of the results reveals one very striking feature, the low Sr content of almost all the dolomitic limestones. Practically all the calcium limestones, except for instance the recent tufa (SL 254) [NG 836 415], have contents of Sr above 100 p.p.m., and the mean of over 200 such limestones is over 700 p.p.m. On the other hand, the mean of over 50 dolomitic limestones ($\text{MgO} > 10\%$) is only 140 p.p.m., with numerous contents below 100 p.p.m., and the higher values occurring in rocks with large insoluble residues. The mean values for the different formations are as follows:

	MgO <10%	MgO >10%
Lewisian	1,500	140
Moine	300	

Shetland Metamorphic	1,200	
Dalradian	1,200	200
Unclassified Metamorphic	1,500	
Cambro-Ordovician	200	60
Ordovician	230	
Lower Old Red Sandstone	150	
Middle Old Red Sandstone	3,000	
Upper Old Red Sandstone	270	180
Calciferous Sandstone	360	170
Carboniferous Limestone	540	130
Jurassic	360	
Cretaceous	200	
Recent	870	

This would appear to substantiate the conclusions of V.M. Goldschmidt (1954, p. 248) based presumably on very few results quoted by W. Noll (1934).

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