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# The limestones of Scotland: chemical analyses and petrography

## Chapter 2 The petrographical examination of limestones and dolomites and the complementary relation of petrographical and chemical study

Limestones and dolomites are composed essentially of the carbonates of lime and magnesia which form the minerals calcite  $\text{CaCO}_3$  and dolomite  $\text{CaCO}_3\text{MgCO}_3$ . The main constituents which occur in the less pure carbonate rocks are oxides or complex oxygen compounds of silicon, aluminium, iron and magnesium and take the form of the minerals quartz and chert, clays, limonite, chlorite and micas. Hydrocarbons and carbonaceous material and sulphide of iron also are often present. Since the carbonates of calcium and magnesium are soluble in warm dilute hydrochloric acid while the other constituents are insoluble or only partially soluble after prolonged treatment, a convenient and rapid way of estimating the purity and approximate composition of the stone is to determine the percentages of lime and magnesia passing into solution in acid, of carbon dioxide evolved, and of the material remaining insoluble. This 'partial analysis' can be supplemented by chemical analysis of the insoluble residue and by determination of the minor constituents of the solution to effect a 'complete analysis' but complete analysis is more systematically carried out as described in pages 8 to 13.

While chemical analysis provides a statement of the amounts of the various oxides present in the stone it does not state in what mineral form they occur. The minerals present, their grain-size and the manner in which they are spatially related form the subject of petrographical examination.

Petrographical examination is carried out by examining under the microscope a thin transparent section of the stone to determine the species, size and proportion of the various minerals and their textural relations and by examining the finely powdered stone to determine more precisely the identity of the minerals. It is difficult to discriminate between calcite and dolomite in thin section owing to the similarity of their appearance and of their reactions to polarized light under the microscope. Discrimination is made by examining thin sections subjected to treatment in Lemberg's solution (Holmes 1921, p. 265) whereby calcite is stained violet, while dolomite remains unstained, or to treatment in solution of silver nitrate followed by immersion in potassium chromate (Wilson 1954, p. 27), whereby calcite acquires an opaque impregnation, dolomite remaining unaffected. Dolomite frequently contains iron carbonate in solid solution and pure dolomite is distinguished from ferriferous dolomite (or ankerite) by remaining unstained when treated with hydrogen peroxide and caustic potash (Hallimond 1925, p. 39) while the ferriferous carbonate takes on an orange stain the depth of which, under controlled conditions, corresponds to the proportion of ferrous carbonate (Taylor 1949, p. 33). Distinction of pure dolomite from ferriferous carbonate is made also by optical examination of the powdered stone (see below).

It is sometimes necessary also to discriminate between the two forms of calcium carbonate, namely calcite and aragonite. When boiled in cobalt nitrate solution aragonite assumes a lilac tint (Meigen's reaction, Holmes 1921, p. 262) while calcite is unaffected; on further treatment, after washing, with ammonium sulphide aragonite is blackened.

The advantage of staining methods is that distinction between the carbonates is made while the minerals maintain their natural association in the rock. This advantage is lost when the rock is powdered but on the other hand precise determination of the optical properties of the minerals can be made when they are isolated in powder form. This method of examination is of unusually easy application to limestones, since calcite which is the predominant constituent is readily removed by solution in cold dilute hydrochloric or acetic acid. Its employment is necessary for the identification of minerals which are present in only minor quantity or as small grains. Examination of the insoluble residue is essential in the examination of limestones which contain clay, because the clay component is often invisible in thin section, and because even when perceptibly present no reliable estimate of its proportion is possible. That clay is an important constituent of a limestone is more readily apparent from the dull and earthy appearance of the stone in hand specimen than from the thin section.

Many limestones are seen in thin section of normal thickness to contain much opaque or obscurely translucent material. Identification of this is greatly aided by examination in reflected light under a binocular microscope, the slide being placed on a black background. The main mineral constituents of limestones which may be studied in this way are pyrite, limonite, graphite, carbonaceous and bituminous matter. Pyrite when visibly crystalline is readily distinguished by its colour, but when in a state of fine subdivision appears grey-black. It can then be distinguished from graphite or carbonaceous matter by the difference in blackness and owing to its superior hardness over carbonate, by its possession of an appearance of relief which is enhanced by the stereoscopic effect of the binocular. The pinkish or reddish tint of limonite contrasts with the yellowish or orange colour of bituminous matter and discrimination between these minerals was found satisfactory after experience had been gained by checking the diagnosis of bitumen by subsequent extraction of the corresponding powder with bitumen solvents and by distillation.

Petrographical examination and chemical analysis are complementary. When only a partial chemical analysis is available, petrographical examination is particularly useful in providing information quickly on the nature and relative proportions of the constituents present besides carbonate, for example, whether they consist predominantly of silica or of clay. Complete chemical analysis in its turn provides useful supplementary information on the identity and proportion of constituents such as clays, the determination of which is sometimes possible but only in general terms by optical study of the insoluble residue; complete mineralogical study of the clay component is possible only by employing X-ray and differential thermal methods of analysis.

Under control by petrographical examination it is possible to compute from the complete chemical analysis of a rock a 'rational analysis' showing its approximate mineral composition in terms of simple mineral compounds. Since the minerals which actually occur in the rock are in general complex compounds such an analysis can rarely approach precision but, particularly in the cases of limestones which are largely composed of carbonates, it may give a valuable indication of the nature of the minor constituent minerals. Some examples of rational analyses of impure limestones are given in the accompanying table. The usefulness of the procedure is noteworthy in the case of the Arden Limestone (SL 140) [NS 524 586], as it shows that the clay component of this rock is mostly quartz which is in such a state of fine subdivision that it cannot be recognized under the microscope.

#### *Rational Analyses of Limestones*

Name	Bilston Burn No. 3	Jenny Pate	Arden (Calmy)	Cementstone	Cementstone	Cementstone
Spec. No.	SL22	SL119	SL140	SL181	SL192	SL193
Slide No.	<a href="#">(S34543)</a> [NT 182 541] (p. 126)	<a href="#">(S34592)</a> [NS 9840 8585] (p. 129)	<a href="#">(S34626)</a> [NS 524 586] (p. 129)	<a href="#">(S34902)</a> [NT 0758 6486] (p. 102)	<a href="#">(S34968)</a> [NS 5221 8014] (p. 104)	<a href="#">(S34969)</a> [NS 5221 8014] (p. 104)
Anal. No.	M17392 (p. 58)	M19721 (p. 60)	M21743 (p. 61)	M24254 (p. 39)	M25784 (p. 41)	M25785 (p. 41)
CaCO <sub>3</sub>	39.98	48.13	68.74	48.53	53.14	49.83
MgCO <sub>3</sub>	25.20	24.61	4.93	22.93	30.22	31.92
FeCO <sub>3</sub>	7.02	8.65	—	4.49	1.90	2.22
MnCOs	0.17	0.51	0.16	0.37	0.19	0.21
Chlorite	—	—	0.11	4.24	4.00	5.69
Kaolinite	—	—	1.96	—	—	—
Muscovite	2.16	4.55	4.07	4.95	2.88	1.84
Quartz	19.61	3.22	15.78	7.84	3.68	1.29
Orthoclase	0.62	—	—	2.12	1.45	3.24
Albite	0.68	1.68	0.89	1.94	0.68	0.84
Limonite	1.18	—	—	—	—	—
Haematite	—	2.46	1.49	1.19	0.82	0.46
Apatite	0.17	0.44	0.27	0.37	0.03	0.23
TiO <sub>2</sub>	0.34	0.20	0.10	0.21	0.11	0.13
FeS <sub>2</sub>	0.93	0.43	0.88	0.03	0.13	0.39

H <sub>2</sub> O excess +	+0.10	—	—	−0.37	−0.31	−0.34
defect −						

Limestones and dolomites being predominantly composed chemically of the carbonates of calcium and magnesium it is possible to compute approximately, even from partial analyses, the proportions of calcite and dolomite and the content of iron carbonate in the dolomite, since lime is present only as carbonate and since the percentage of carbon dioxide remaining after satisfaction of lime, puts limits to the relative proportions in which magnesia and iron are combined as carbonate. Since the optical properties of the carbonates containing magnesia and iron vary regularly with the composition it is possible to deduce the approximate percentage of iron carbonate in a ferriferous dolomite from its refractive index. During the petrographical examination of the series of Scottish limestones opportunity was taken to compare estimates of the composition of the dolomites by these two methods. The results are tabulated in the accompanying table. Since in most of the analyses iron is expressed as Fe<sub>2</sub>O<sub>3</sub> allocation of CO<sub>2</sub> to magnesium and iron when insufficient to satisfy both is uncertain and limits of composition are therefore given in the table. Considering that the refractive index determinations were made on minute quantities of minerals from one hand specimen while the chemical analyses were made on fractions from large and often composite samples the agreement shown between the measured refractive index and that deduced from the computed composition (Hawkes and Smythe 1935, p. 71) is good. In general for the more ferriferous dolomites the observed index is lower than this deduced value, a conclusion reached also by Smythe and Dunham (1947, p. 67) in a study of the ankerites from the north of England. It appears therefore that the refractive index test, which can be carried out in a short time, is a reliable indication of pure or only slightly ferriferous dolomite, but tends to give a low indication of the content of ferrous carbonate as this increases.

Many of the limestones described in the series of Scottish limestones belong to the class of metamorphic rocks, that is, they have been changed by the action of heat and stress since their consolidation as rock. While their chemical composition as shown by complete analysis may have been little changed except for the diminution or disappearance of carbon dioxide, their mineral constituents have often been transformed, the sandy and clay components of the original rock having combined with the lime and magnesia to form silicates and aluminosilicates which are insoluble in acid. In such rocks the original sedimentary structure has in general disappeared and the stone has a crystalline appearance. Such limestones are characteristic of the Lewisian, Moinian and Dalradian formations, but locally limestones of other formations have been similarly transformed by the heat and gases from igneous intrusions. For example, the Charlestown Main limestone of Carboniferous Limestone age (p. 117) has been greatly altered by a quartz-dolerite sill at Chapel, Kirkcaldy, and so much boron derived from the gases accompanying the sill has been taken into combination with the limestone that it fluxes in the kiln. In this case the value of the stone has diminished because of the metamorphism. In other cases the value may have increased because of the development of some mineral of value, such as brucite, or of the production of a mineral such as serpentine, which gives the rock a handsome appearance as a decorative stone, or of tough minerals which render it more resistant in use as roadstone.

The metamorphic character of a limestone is more readily recognized by petrographical examination than by chemical analysis. Moreover the latter, to show the true content of lime and magnesia, must be a complete analysis since much of these oxides is combined with silica in insoluble minerals. It may happen also that just as chemical analysis directs attention more effectively than ordinary petrographical examination to the clay component of a limestone, so may petrographical study indicate by the recognition of an unusual mineral the presence of some element such as boron which would not be looked for in an ordinary 'complete' chemical analysis.

Thus in assessing the useful reserves of limestone it is important to recognize the complementary nature of chemical and petrographical examination. Not only is it advisable to estimate the volume of stone and its content of soluble lime but also to study its mineral composition and, particularly in an area where igneous intrusions are liable to occur, its geological relations, both of which may have important influence on the use to which the stone may be put and on the reserves utilizable for a particular purpose.

## References

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### Compositions and refractive indices of Ca-Mg-Fe carbonates

Page ref.	Spec. no. SL	Rock section No. S	Calculated from chemical analysis				Refractive index		Notes
			CoCO <sub>3</sub> *	MgCO <sub>3</sub> *	(FeMn)CO <sub>3</sub> *	(CaFeMn)CO <sub>3</sub> /total carbonate × Calculated 100	Observed	Observed	
93	(SL 177)	<a href="#">(S34846)</a> [NC 436 572]	52.2	41.7	nil	nil	1.679	1.680	* = weight per cent
93	(SL 176)	<a href="#">(S34838)</a> [NC 372 626], <a href="#">(S34839)</a> [NC 372 626], <a href="#">(S34840)</a> [NC 372 626], <a href="#">(S34841)</a> [NC 372 626], <a href="#">(S34482)</a>	53.6	43.6	0.3	0.7	1.680–	1.679–1.680	
80	(SL 87)	<a href="#">(S34842)</a> [NM 9832 5421] <a href="#">(S34843)</a> [NC 384 649], <a href="#">(S34844)</a> [NC 384 649], <a href="#">(S34845)</a> [NC 384 649]	47.6	38.6	0.3	1.5	1.680+	1.681	
92	(SL 175)	<a href="#">(S34844)</a> [NC 384 649], <a href="#">(S34845)</a> [NC 384 649]	52.2	41.7	0.7	1.7	1.681	1.679–1.680	

129	(SL 140)	<a href="#">(S34626)</a> [NS 524 586]	68.7	4.9	0.2	2.9	1.682	1.682	
100	(SL 91)	<a href="#">(S34486)</a> [NS 4083 7782]	47.3	31.5–33.4	0–4.3	0–5.9	1.679–1.684	1.680	Clay and biotite present
104	(SL 221)	<a href="#">(S35075)</a> [NT 790 368]	53.5	39.0	1.5	3.3	1.682+	1.680	
87	(SL 75)	<a href="#">(S34515)</a> [NJ 263 328]	74.9	1041	0.55	4.1 or less	1.683	1.682	Micas present
130	(SL 120)	<a href="#">(S34593)</a> [NS 9722 8572]	51.0	37.4	1.9	4.1	1.683	1.682	
104	(SL 192)	<a href="#">(S34968)</a> [NS 5221 8014]	53.2	30.3–31.7	0–2.1	0–5.6	1.679–1.684	1.681–2	Sericite and chlorite present
104	(SL 193)	<a href="#">(S34969)</a> [NS 5221 8014]	49.8	31.9–33.7	0–2.4	0–6.1	1.679–1.685	1.681	Sericite and chlorite present
105	GS10	<a href="#">(S33200)</a> [NS 610 799]	46.5	29.0–31.0	0.5–3.2	1.6–8.8	1.680–1.687	1.683	
103	(SL 200)	<a href="#">(S35065)</a> [NY 592 975]	79.2	12.6–10.4	0.5–3.4	3.1–21.9	1.682–1.698	1.683–5	Dolomite subordinate to ankerite with ■ < 1.702 Varies slightly above and below 1.690
101	(SL 31)	<a href="#">(S34453)</a> [NO 6133 1128]	53.2	37.3	6.5	12.9	1.690	1.690	
117	(SL 8)	<a href="#">(S34442)</a> [NT 1292 8450]	71.8	24.4	3.35	14.0	1.691	1.690–5	
102	(SL 181)	<a href="#">(S34902)</a> [NT 0758 6486]	48.5	22.9	4.8	15.3	1.692	1.681–1.696	Mostly about 1.686 ■ appears to increase with coarseness of grain
125	(SL 233)	<a href="#">(S35236)</a> [NO 5315 0180]	50.1	34.4	8.5	17.4	1.694	1.685–1.715	
112	(SL 37)	<a href="#">(S34458)</a> [NO 4054 0773]	52.9	35.6	9.6	18.7	1.695	1.695	
126	(SL 44)	<a href="#">(S34533)</a> [NT 345 573]	50.3	32.0	8.9	19.1	1.695+	1.690	

126	(SL 22)	<a href="#">(S34543)</a> [NT 182 541]	40.0	25.2	7.2	19.6	1.696	1.689	
112	(SL 34)	<a href="#">(S34456)</a> [NO 4848 0427]	54.6	32.0	9.5	20.2	1.696+	1.695-8	
131	(SL 7)	<a href="#">(S34441)</a> [NS 9879 9829]	51.0	32.1	9.65	20.4	1697	1.695	
115	(SL 21)	<a href="#">(S34542)</a> [NT 171 543]	62.2	5.8-5.2	1.5-2.4	19-28	1.695-1.703	1.685-1.695	Mostly about siderite present
129	(SL 119)	<a href="#">(S34592)</a> [NS 9840 8585]	48.1	24.6	92	24.1	1.700	1.695	Occasionally higher
101	(SL 28)	<a href="#">(S34450)</a> [NO 6113 1133]	52.1	33.0-32.0	12.1-13.4	23.8-26.3	1.700-1.702	1.697	Often a little higher
112	(SL 64)	<a href="#">(S34553)</a> [NT 4497 8029]	60.2	25.4	11.2	27	1.702	1.688-1.697	
101	(SL 29)	<a href="#">(S34451)</a> [NO 6099 1147]	48.2	28.4	12.9	28.0	1.703	1.700	Mostly 1.700 but varies to 1.715
118	(SL 50)	<a href="#">(S34465)</a> [NO 2952 0584]	58.8	29.1-27.7	13.1-14.1	27.6-29.3	1.702-1.705	1.697	Dominant value; ■ reaches 1.705
128	(SL 118)	<a href="#">(S34591)</a> [NT 0803 9044]	40.4	23.2-20.9	9.7-12.9	26.4-32.4	1.701-1.707	1.702	
102	(SL 33)	<a href="#">(S34455)</a> [NO 5312 0668]	35.0	20.1	12.5	34.5	1.710-	1.700	Varies slightly below 1.700; siderite present
101	(SL 30)	<a href="#">(S34452)</a> [NO 6125 1131]	43.9	25.2	17.2	35.5	1.710+	1.690-1.705	Mostly between 1.690 and 1.700: siderite present
105	(SL 172)	<a href="#">(S34856)</a> [NT 2155 8637]	53.1	26.1	19.3	38.5	1.712	1.708	