Some metasomatic calc-magnesian silicate rocks from Connemara, western Ireland: mineralogical control of rock composition

BERNARD E. LEAKE

Department of Geology, University of Glasgow Glasgow, G12 8QQ, Scotland

Abstract

Chemical analyses for 33 major oxides and minor elements are reported for a series of 26 associated metasediments that range from staurolite-garnet schists through similar pelites with graphite to schists with varying contents of actinolitic amphibole and diopside-rich calc-magnesian silicate rocks. The calc-magnesian silicate rocks cannot be matched with any likely original sediment and have probably formed by metasomatism of pelites by processes similar to those that produce rodingites. The presence of graphite, gradation into pelites, and the positive correlation of Ti and Niggli al-alk support a part sedimentary parentage for the calc-magnesian rocks. Ca, Mg, Cr, and Ni (maxima 13.7% CaO, 24.2% MgO, 2470 ppm Cr and 620 ppm Ni) were added from solutions derived from nearby ultramafic rocks serpentinized during static regional metamorphism, which caused andalusite and cordierite growth in some of the associated pelites.

Although the original sedimentary composition and the composition of the metasomatizing fluids were important in determining the chemical composition of the metasomatic rocks, the stable amphibole and pyroxene mineralogy in the calc-magnesian silicate rocks was no less important. These rocks are an example of the partial mineralogical control of the composition of metamorphic rocks.

It is proposed that a characteristic feature found in many sedimentary rocks, but not in igneous rocks, is a marked positive correlation of Ti and Niggli al-alk.

Introduction

In the Dalradian succession south of Cornamona, Co. Galway, Ireland (Fig. 1), is a series of actinolitic amphibole-diopside-biotite or phlogopite-plagioclase-quartz-graphite schists that grade into graphitic pelites with staurolite and garnet. This paper tabulates the chemistry of these rocks and tries to deduce the origin of the amphibole- and pyroxenebearing rocks. The study was initially undertaken to determine whether the present rocks were derived by metamorphism of dolomitic pelites or whether their origin involved basic or ultrabasic igneous material mixed with sedimentary matter. The results obtained point to the operation of metasomatic as well as original sedimentary processes, the rocks being produced by the interaction of solutions, similar to those that produce rodingites, with graphitic pelites.

The samples come from a graphitic schist series that contains some serpentine and ultramafic lenses, rare thin calcite marbles, and thin banded quartzites, in addition to calc-magnesian schists rich in actinolitic amphibole and diopsidic pyroxene. This succession (Fig. 1) lies north of a thin staurolite-garnettwo mica pelite that itself lies north of a coarse pebbly grit. The whole area has been mapped in detail on the scale of 1:10,560 with every outcrop examined and recorded; Figure 1 is a simplified geological map. The calc-magnesian rocks are interlayed with graphitic schists and have transitional boundaries both across strike and along strike. The schistosity is poorer in the calc-magnesian rocks, due to late rather random growth of actinolitic amphibole and clinopyroxene. Some of the rocks have a banded appearance due to differential weathering, but the contacts between the bands are almost always gradational (e.g. samples BL3611-7). Clinopyroxene-rich clots sometimes occur in amphibole-rich schist (e.g. BL3617), and patches of garnet-rich rock (e.g. BL3623) occur occasionally. Although ultramafic lenses occur in the area, these are always distinct with sharp contacts. There is no gradation into the studied rocks, nor do



Fig. 1. Geological map of part of the area south of Cornamona, Co. Galway, Ireland showing the sample locations. Mapped by the author.

the calc-magnesian rocks occur in flattened or unflattened tectonic lenses.

The highest grade of metamorphism reached by these rocks was post- F_2 and pre- F_3 folding just at the sillimanite isograd (Yardley *et al.*, 1980), with the pelites in the present area being staurolite–garnet schists with rare kyanite (Fig. 1). The staurolite and kyanite pre-date a strong static metamorphism that produced cm-sized cordierite and andalusite porphyroblasts in a patchy distribution in the pelites. It was during this post- F_3 metamorphism that the amphibole- and pyroxene-bearing rocks crystallized, for these minerals have random arrangement.

Geochemistry

Carbonate-pelite mixtures

Figures 2 and 3 show that the analyzed rocks (Tables 1 and 2) plot in a cluster extending from the field

of pelites (defined by over 100 Connemara pelite analyses given in Senior and Leake, 1978), in which representative Connemara pelites plot towards a composition that lies between magnesite and dolomite. These plots show that neither pure limestone (Niggli c 100) nor pure magnesite (c zero, Niggli mg 1.0) was involved as a component of the original sedimentary mixture. If carbonate-pelite mixtures were involved, then from the c-mg plot of Figure 2 they must have been roughly equal proportions of dolomite and magnesite mixed with variable amounts of pelite. Such a sediment would have been a most curious one, in that the proportion of dolomite to magnesite was rather invariable and also because primary magnesite is not at all usual in sedimentary rocks; indeed, Johannes (1969) supposes that magnesite almost always originates by metasomatism.

Moreover, most of the samples contain as much SiO_2 , or even more, than typical Connemara pelites which have less than 5% total CaO + MgO (Fig. 4). Thus average Connemara pelite has 55.39% SiO_2 and







Fig. 3. Plot of Niggli al-alk against c for the analyzed rocks plus published Connemara pelites.

4.26% CaO + MgO (Senior and Leake, 1978), whereas the present samples (Table 1) average 60.08% SiO₂, or if only those samples with more than 10% CaO + MgO are considered, then the SiO₂ averages 54.95% and the CaO + MgO 22.34%. This is an insignificant silica change despite 18% more CaO + MgO than in an average pelite. Even if the SiO₂ had been increased due to complete decarbonation, no mixture of carbonate with pelite can be as rich or richer in SiO₂ either before or after decarbonation than the same pelite alone, because of the residual CaO + MgO content in the mixture. The CaO/MgO ratio against SiO₂ (Fig. 4) suggests variation between pelite, tremolite, and diopside, not pelite and carbonate. Complete decarbonation is not an attractive theory because nearby stable calcite marble is common in the area (Fig. 1) and decarbonation is not significant.

Further evidence against the carbonate-pelite mixture hypothesis is obtained from the trace elements Ni and Cr, both of which are present in sedimentary carbonate deposits in very low amounts whereas pelites commonly contain much more Ni and Cr. Mixtures of pelite and carbonate should have progressively lower contents of Cr and Ni as the carbonate content increases. Figure 2 shows that this does not occur. The average Ni and Cr contents of the eleven samples that are amphibole- and pyroxene-free are 88 ppm Ni and 128 ppm Cr, compared with 166 ppm Ni and 688 ppm Cr for the average of the 16 amphi-

BL -	3612A	3613	3615	3616	3621	3622	3623	3625	3632	3633
SiO2	58.06	57.41	60.55	52.64	55.09	56.32	56.81	62.11	51.71	49.55
A1203	19.03	19.41	14.38	9.66	20.91	18.71	15.30	18.32	19.43	20.05
TiO2	0.94	1.14	0.81	0,72	0.95	0.83	1.39	0.78	0.96	0.87
Fe203	2.55	2.77	2.59	2.51	2.69	2.66	1.16	2,48	2.86	2.64
Fe0	5.62	5.34	6.48	6.11	6.70	6.62	15.22	5.17	4.86	5.06
MgO	2.93	2.78	5.38	14.04	3.67	3.92	2.32	3.01	6.64	6.35
Ca.O	0.90	1.20	2.00	5.80	1.26	2.61	5.08	1,12	2.76	2.05
NB20	1.46	2.94	1.94	0.27	1.13	2,36	1.74	2.00	1.45	1.39
K20	4.38	3.59	3.36	2.45	4.57	3.32	2.07	3,86	7.14	7.12
MnO	0.08	0.06	0.21	0.26	0.12	0.15	0.40	0.12	0.08	0.07
P205	0.11	0,13	0.18	0.18	0.10	0,12	0.29	0,10	0.14	0.12
H2O+	3.98	3.24	1.58	4.20	2.82	2.78	2.63	1.14	1.02	2,40
S	0.10	0.09	0.07	0.01	0.14	0.10	0.02	0.01	0.43	0.39
C	0.14	0.00	0.14	1.81	0.14	0.40	0.00	0.00	0.32	2,32
Total	100.18	100.10	99.67	100.66	100.29	100.50	100.43	100.22	99.80	100.34
Fe203	8.93	B.72	9.81	9.32	10.15	9.63	15.89	8,24	8.27	0,28
Clppm	117	130	224	176	114	130	128	94	165	150
V	354	333	352	345	363	348	371	306	355	348
Cr	65	76	125	560	97	72	53	87	129	96
Mr.	48	38	100	425	43	47	68	37	75	41
Cu	25	40	46	8	66	55	12	14	97	90
Zn	134	122	141	150	146	143	102	123	130	147
Ga	50	20	23	19	30	28	22	29	25	30
Rb	160	126	167	114	178	163	83	177	210	227
\mathbf{Sr}	114	199	198	92	156	292	225	143	341	337
X	31	28	23	21	30	18	22	22	15	12
Zr	-98	125	72	67	112	104	142	88	121	91
Nb	15	18	12	11	16	17	17	14		16
Cs	14	15	16	14	16	16	18	14	16	17
Ba	1885	1850	940	828	1180	814	681	1100	2375	2775
La	49	51	36	27	52	43	47	41	43	42
Ce	110	123	89	76	129	105	160	102	104	91
Pb	43	37	41	17	37	46	69	38	57	54
Th	21	13	10	11	17	15	5	20	12	14
U	8	4	5	9	12	7	5	1	B	7

Table 1. Chemical analyses of amphibole- and pyroxene-free metasediments

bole- or pyroxene-bearing samples, though there is a wide range of values in this group. These values compare with the average of 6 ppm Ni and 15 ppm Cr for 29 unsegregated siliceous dolomites forming the green Connemara marble (Leake et al., 1975).

The chemistry of the amphibole-pyroxene rocks is therefore extremely difficult to explain in terms of possible sedimentary parents. The possibility that the failure of the silica to fall with increase of carbonate was due to a coincidental increase in detrital quartz with the increase in carbonate is ruled out by the Cr and Ni results. Quartz is extremely deficient in these elements, and very low Cr and Ni values should then be found in the amphibole-pyroxene rocks, which is not the case.

Pelite-basic igneous mixtures

An alternative possibility is that the amphiboleand pyroxene-bearing rocks were derived from a mixture of graphitic clay with basic volcanic ash or detrital fragments of a basic igneous rock. However, for this to be so, the original sediments should have contained either some layers or rock fragments made almost entirely of augite with orthopyroxene (olivine is excluded by the silica content of the rocks; Fig. 6), because analyses BL3626 to BL3629 (Table 2) have very low Niggli al-alk values (Fig. 3), and very low $Al_2O_3(5.19 \text{ to } 2.13\% \text{ } Al_2O_3)$; *i.e.* the plagioclase con-

Explanation to Tables 1 and 2

- Graphitic quartz schist with albite and Kf porphyroblasts and BL3611 a little phlogopite, sulphide and actinolitic amphibole. yards SSW of Bench Mark 34.4 that is on a bridge on the Cornamona-Glenlusk boundary. 100
- BL3612A Quartz-muscovite-biotite graphite schist with rare small garnets and relic biotite crystalloids lying across the schistosity. Location as 3611. BL3612B As 3612A but with amphibole and pyroxene clots.
- BL3612 AS Joite, with augminibile and pyroteche closs. BL3613 Albite, with quartz inclusions in a relict S_i, muscovite-biotite-quartz-rare staurolite and tourmaline schist. Location as 3611.
- BL3614 Quartz-actinolitic amphibole-diopside-phlogopite-graphitesulphide schist. As 3611. BL3615 Bictite-muscovite schist with quartz folia, oligoclase over-
- growing puckered graphite trails, and rare garnet and tourmaline. Location as 3611. BL3616 Phlogopite-quartz-feldspar-graphite schist with a little
- prehnite in biotite and rare Kf veins. As 3611. BL3617 Diopside-rich rock with completely sericitised feldspar, a
- stittle actinolitic amphibole, quartz, leucoxenised sphere, graphite and sulphide. As 3611. Quartz-rich-amphibole-sericitised feldspar schist with a
- BL3618 little sulphide and biotite. 70 yards SSW of the first o of Cornamona (townland) as written on sheet 39, Co. Galway 1:10,560.
- BL3619 Diopside-actinolitic amphibole phlogopite-quartz-Kf-sericite schist with graphite, sulphide and sphene. 340 yards SSW of the last a of Cornamona (townland) as written on sheet 39, Co. Galway 1:10,560.
- BL3620 Diopside-actinolitic amphibole phlogopite-Kf-sericitised feldspar schist with graphite, sulphide, quartz and sphene. As 3619.
- BL3621 Biotite-muscovite-quartz-plagioclase schist with a little garnet, sulphide and graphite. As 3619.
 BL3622 Biotite-quartz-oligoclase-sericitised plagioclase-garnet
- schist with graphite, sulphide, leucoxenised ilmenite, green biotite and chlorite. As 3619.
- BL3623 Quartz-biotite-garmet-plagioclase-sericite schist with apatite and ilmenite. As 3619.
- Quartz-actinolitic amphibole-diopside-phlogopite-Kf-sericite BL3624 with a little graphite and sulphide. As 3619. BL3625 Biotite-muscovite-quartz-plagioclase-garnet schist with a
- BI5029 BI0themasource-quarts-plaghorize-galactic solist with little staurolite. As 5619.
 BL3626 Actinolitic amphibole diopside schist with decomposing diopside. 35 yards east of the last h of Whitegoat Rock North as written on sheet 39, Co. Galway 1:10,550.
 BL3627 Actinolitic and amphibole-diopside schist with a little whom to a 5606 at Rock
- chlorite. As 3626. BL3628A Actinolitic amphibole-rich schist with sericitised feldspar
- and a little quartz, magnetite and graphite. As 3626. BL3628B Similar to 3628A.
- Actinolitic amphibole rock with rare phlogopite and sulphide. BL3629
- As 3619. BL3630 Actinolitic amphibole altered clinopyroxene-Kf-sericite schist with accessory sphene. 180 yards east of the last of Whitgoat Rock North as written on sheet 39, Co. Galway 180 yards east of the last h 1:10,560.
- BL3631 Quartz-actinolitic amphibole sericite-graphite schist with As 3630.
- accessory sulphide, sphene, chlorite, thin Kf veins. BL3632 Biotite-plagioclase-quartz-Kf rich-graphite schist with late prehnite and some sulphide. 180 yards east of Sallow Bush
- island.
- BL3633 Biotite-quartz-Kf-plagioclase-graphite schist with accessory sulphide, prehnite and epidote. As 3632.
 BL3634 Diopside-actinolitic amphibole sericite-Kf-quartz-graphite
- schist with accessory sulphide, sphene and calcite. 330 yards south of the last a of Cornamona as written on sheet 39, Co. Galway 1:10,560. BL3634A As 3634 except rather more diopside.
- BL3638
- Amphibole-quartz-phlogopite-sericite-graphite schist. 360 yards south of the m of Cornamona as written on sheet 39, Co. Galway 1:10,560.
- BL3153 Actinolitic amphibole-diopside-quartz-Kf-sericite-graphite schist with accessory sphene and sulphide. By the third t of Whitegoat Rock North as written on sheet 39, Co. Galway 1:10.560.

All analysis have been carried out by XRF analysis using the method of Leake <u>et al</u>. (1969) except for FeO, H₂O and C which were determined by wet methods by A.Kemp. Fe₂O₃ is total iron as Fe₂O₃.

tent would have been insignificant. Such layers or fragments, whether tectonic or detrital, are absent. Such an ultramafic volcanic ash or detrital ultramafic material is so unusual as to be implausible. The clustering of so many analyses so closely around the composition of actinolitic amphibole (Fig. 2) requires

LEAKE: CALC-MAGNESIAN SILICATE ROCKS

Table	2.	Chemical	analyses	of an	phibole-	and	pyroxene-	bearing	rocks
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BL -	3611	3612B	3614	3617	3618	3619	3620	3624	3626	3627	3628A	3628B	3629	3630	3631	3634	3634A	3138	3153
Siloo	80,18	53.55	59.55	54.86	76.01	55.22	53.88	58.11	53.34	51.31	51.45	55.83	52.35	52.08	63.65	56.66	58.10	59.76	56.76
A1-07	6.36	10.40	10.90	9.50	7.03	11.75	13.05	11.61	3.60	5.19	3.97	3.02	2.13	11.21	12.25	13.05	11.96	11.22	11.91
Ti00	0.36	0.41	0.47	0.40	0.60	0.43	0.49	0.44	0.07	0.13	0.08	0.02	0.16	0.44	0.53	0.41	0.41	0.57	0.62
FeoOz	1.62	0.22	1.90	0.41	1.92	1.32	1.23	2.03	1.07	1.24	1.62	0.65	1.90	0.73	2.37	1.24	1.33	1.10	1.04
Felo	1.00	5.14	3-12	4.30	3.45	3.53	3.97	2.90	6 22	5.67	6.30	6.30	5.74	4.16	3.35	3.38	3.28	4.14	3.38
MaO	2.07	11.27	7.22	11.79	4.02	9.93	10.20	8.86	19.55	18,57	24.25	21.04	22.71	11.11	6.28	9.18	9.01	8.77	8.72
CaO	0.91	10.60	6.56	12.02	3.68	9.81	9.01	7.80	13.21	13.75	10.31	11.07	10.23	10.85	5.62	8.94	9.93	7.94	7.55
NaoO	1.03	1.18	4.30	1.41	1.04	0.43	0.57	0.55	0.14	0.48	0.16	1.09	0.07	4.44	0.53	0.47	0.68	0.95	0.62
Kan	3.67	2.54	3.42	2.78	1.30	4.98	4.57	4.80	0.24	0.20	0.04	0.05	0.01	3.73	3.50	4.35	3.45	2.64	3.68
MnO	0.01	0.18	0.35	0.18	0.09	0.07	0.10	0.42	0.31	0.27	0.26	0.42	0.26	0.17	0.15	0.09	0.13	0.17	0.12
PoOr	0.28	0.20	0.20	0.20	0.12	0.18	0.13	0.39	0.05	0.23	0.17	0.06	0.23	0.10	0.28	0.28	0.14	0.18	0.19
Hall	1.16	3.90	1.44	2,18	1.55	1.06	2.34	2.06	2.34	2.70	0.78	0.78	3.58	1.98	1.38	1.54	1.58	2.89	3.88
S	0.27	0.06	0.41	0.12	0.02	0.26	0.30	0.36	0.01	0.01	0.21	0.01	0.40	0.01	0.18	0.18	0.09		
č	1.58	0.36	0.06	0.18	0.00	1.34	.0.80	0.24	0.00	0.00	0.50	0.00	0.00	0.00	0.14	0.51	0.40	00.07	00 47
Total	100.50	100.00	100.20	100.33	100.83	100.31	100.64	100.57	100.15	99.75	100.10	100.34	99.77	101.01	100.21	100.28	100.49	99.91	98.41
Feo03	2.73	5.93	5.70	5.20	5.76	5.25	5.64	5.26	8.00	7.56	8,62	7.67	8.29	5.35	6.10	5.07	4.98		
() mm	116	166	160		85	1/18	165	146	93	175	131	97		188	135	187	115		
T ppm	00	213	315	109	271	74	198	278	108	184	148	51	123		334	275	250		
Cm	54	52	80	73	369	46	78	51	1420	1381	2418	2272	2470	59	87	79	71		
NA	20	13	32	13	85	30	31	29	362	317	468	620	446	39	60	39	35		
Chi	66	31	79	29	28	70	71	64	20	61	62	21	55	17	97	63	42		
Zn	53	131	109	132	83	76	110	109	118	125	104	84	105	97	85	75	85		
Ga	15	16	19	14	14	15	18	18	4	7	6	3	6	16	15	13	12		
Rb	137	114	140	115	86	173	186	172	10	3	1	1	1	153	161	130	129		
Sr	170	345	270	346	313	259	230	220	29	31	22	15	21	237	217	270	278		
Y	15	17	16	16	19	21	16	16	2	3	2	4	3	20	18	18	14		
Zr	22	40	45	49	210	65	41	26	0	15	2			77	46	44	55		
Nb	9	10	11	9	12	13	11	8	8	7	7			11	12	11	10		
Cs	7	7	9		9	9	8	8	3		2	4		8	9	9	4507		
Ba	1297	866	1500	771	420	2310	2845	3204	78	22	2	44		1734	1840	1755	1527		
La	6	21	23		20	27	23	24				5		23	24	24	21		
Ce	18	61	55	55	75	52	49	44	36	39	48	43	41	56	62	12	20		
Pb	47	29	37	15	34	58	62	41	26	43	52	17	62	25	22	12	10		
Th	6	7	11	7	9	11	5	12	7	2	2	5	1	9	14	9	9		
U	17	8	11	10	7	7	14	10	1	1		2	3	б	14	2	ſ		

a regularity in the ratio of augite to orthopyroxene that is beyond credibility in a tuffaceous or detrital rock. plagioclase was not important in the original sediment, even for those samples with Niggli al-alk exceeding 5. If plots are made of many pelitic and semipelitic series, characteristic features differentiate

There is, moreover, independent evidence that





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Fig. 5. Plots of Niggli ti against al-alk. (A) Three series of Ordovician sediments from Wales (Bjørlykke, 1971). (B) Cornamona and other Connemara analyses. (C) Karroo dolerites (Walker and Poldervaart, 1949). (D) Western part of the Galway Granite; analyses from Wright (1964), Claxton (1971), Aucott (1966), and Leake (1974). Note scale change of al-alk from A and B (sediments) to C and D (igneous rocks).

these rocks in general from rocks of igneous origin, because the sediments have a negative correlation of al-alk with c (Leake, 1969) and a positive correlation of al-alk with ti. The latter indicates that the Ti is mainly in the clay minerals (*e.g.* Lange, 1970; Senior and Leake, 1978), of which al-alk is a good quantitative measure. If plagioclase becomes a major contributor to the sediment, al-alk increases especially if calcic plagioclase is involved, but Ti should not increase. Thus Figure 5A shows that for three series of Welsh Ordovician sediments varying from grits, ashy shales, and mudstones to calcareous shales, a marked correlation of ti and al-alk exists even though some of the sediments contain some detrital feldspar (Bjør-

lykke, 1971). Clearly, the dominant source of the Ti and the excess al-alk lies in the clay mineral content of the sediments. Consequently plots of al-alk against ti for igneous series, both acid and basic as exemplified by the Galway Granite and Karroo Dolerites (Fig. 5C, D), contrast with typical sediments in showing very low degrees of correlation of ti and al-alk. Increase in al-alk in igneous rocks is mainly controlled by the contents of calcic plagioclase, modified by the presence and abundance of biotite.

The present samples (Fig. 5B) give a marked positive correlation of ti and al-alk, revealing a quite unmistakable 'sedimentary trend' confirmed by the very high al-alk values which pelitic sediments display, values far in excess of those found in typical igneous rocks.

Accordingly, probably the present rocks were originally sediments, as is also indicated by their graphite content and by the field evidence of continuous gradation into graphitic pelites. The view that the diopside and actinolitic amphibole-bearing rocks were originally mixtures of graphitic pelite and volcanic ash or detrital or tectonically emplaced basic igneous material is rejected.

Metasomatism

Because of the incompatibility of the geochemistry with isochemical metamorphism, the composition of the samples might be the result of metasomatism of original carbonaceous pelites. In the calc-magnesium-rich rocks pyroxene and amphibole dominate the composition and it is possible that their metasomatic growth controlled or at least greatly influenced the rock composition.

Figure 6 supports this interpretation, because many of the pyroxene-bearing samples plot nearly on a line that if extended would pass through either pure diopside or dolomite. But from Figure 4 it has already been deduced that dolomite cannot have been a major constituent of the variation, so that Figures 4 and 5 are best explained by the rock compositions being controlled by three constituents: pelite, diopside, and an amphibole whose composition is a little less magnesian than tremolite, *i.e.* actinolite. Note that mixtures of dolomite and magnesite would form a broad band across the periphery of the plot, and yet the analyzed samples fall in a narrow segment whose extremes are defined by pyroxene and amphibole.

This interpretation is also supported by Figure 6, in which the analyzed rocks show decreasing Niggli si down to that found in actinolite and diopside but not extending to lower values approaching the carbonates on the left-hand side of the figure. If it is accepted that the occurrence of pelites with layers of detrital actinolite and diopside is an unacceptable possible sediment, then clearly these rocks have their compositions controlled by the stable actinolitic amphibole-pyroxene assemblage.

The most probable original rock, in view of the bedded nature of the series, was a graphitic pelite that has been soaked by Ca- and Mg-bearing solutions, presumably derived from the serpentinization of the associated ultramafic rock now present as serpentine-talc rocks. Figure 2 strongly supports this interpretation, as the Ni and Cr values of the amphi-



Fig. 6. Plots (weight %) of CaO against MgO and Niggli fm against si for the analyzed samples and published Connemara pelites.

bole- and pyroxene-bearing samples show a very wide and erratic variation, with much higher values for some of the samples (BL3628B has 2272 ppm Cr and 620 ppm Ni) than any normal sediment—a typical pelite has about 100 ppm Cr and 70 ppm Ni (Taylor, 1965, p. 170), an order of magnitude less. It is not known what controls the Cr and Ni contents, but Figure 2 shows that the samples with the highest Cr values also have the highest Ni values, and both elements could plausibly have been derived from ultramafic rock during serpentinization. No other source is evident.

Discussion

If the metasomatic interpretation is sound then at least some elements can be expected to show interrelationships that are the result of two quite different processes—sedimentary on the one hand and metasomatic on the other. This may be the explanation for Figures 7 and 8, in which some elements show two rather different trends. The low Cr and Ni values



Fig. 7. Plot of wt% CaO against ppm Sr and Ba. Very low Sr and Ba in the most metasomatized samples suggest removal of these elements. Published analyses of Connemara pelites from Leake (1958) and Evans (1964).

are similar to sediments, in which Cr and Ni are often contained in clay mineral structures; but the high Cr and Ni values are widely separated and suggest the operation of a different process involving the massive addition of these elements. Likewise the relationship of Rb and K with al-alk is suggestive of one clustering dominated by presumably sedimentary processes and another controlled by depletion. In Figure 7 the normal positive association of Sr with Ca is evident in the normal pelites which plot from 0-4% CaO; the metasomatic rocks scatter and do not follow the same trend.

In each plot (Figs. 6, 7, and 8), the same five samples, BL3626-9, show either depletion (Rb, K, Ba, and Sr) or the most pronounced enrichment (Ca, Mg, Ni, and Cr), indicating that the most pronounced metasomatism is recorded in these samples, which are almost entirely actinolitic amphibole (82–99%) with up to 16% pyroxene. These are the extreme development of the putative metasomatic calc-magnesian silicate rocks whose compositions are dominated by a stable mineralogy of amphibole and pyroxenes. These minerals have rejected those elements such as Rb, K, and Ba which do not easily enter amphibole and pyroxene, and accepted those elements such as

Ca, Mg, Ni, and Cr that readily enter the amphibole and pyroxene structures. The role of Sr is less clear, as this element can enter amphiboles and pyroxenes in moderate amounts. The paucity of Sr may be a reflection of impoverishment in the metasomatizing solutions derived from the ultramafic rock, a factor that could also be important for Rb, K and Ba, elements that are not abundant in ultramafic rocks. Rb, K, and Ba show a close coherence and are richest in the samples containing significant biotite and (or) K-feldspar. These minerals provide sites for these elements, which were presumably originally present largely in the pelites, or have been added by solutions which obtained them from nearby pelites. Some evidence supports enrichment of Ba in some samples, because excluding the five samples depleted in Ba mentioned above, the remaining 22 samples average 1568 ppm Ba, whereas Senior and Leake (1978) have shown that typical pelites in Connemara average 781 ppm Ba.

The whole process is an instance of the partial mineralogical control of the chemical composition of a metamorphic rock (Leake, 1972).

If the above interpretation is correct, material rich in Ca, Mg, Ni, and Cr must have left the ultramafic rocks, presumably during serpentinization, while the metamorphic grade was high enough for amphibole and pyroxene crystallization elsewhere, so that lowgrade minerals sometimes found in rodingites, such as prehnite, did not form. The origin of the Ca is particularly interesting. During the serpentinization of ultrabasic and ultramafic rock, rodingites can form by loss of Ca from the ultramafic rock, even though the ultramafic rock may contain extremely little Ca, mostly in diopsidic augite (e.g. Challis, 1965). This is because Ca does not enter the structures of serpentine minerals. Ca is therefore removed in solution (Coleman and Keith, 1971) during the serpentinization of the pyroxene, resulting in serpentinite that is commonly essentially Ca-free. In total, the amounts of Ca removed during serpentinization should generally be less than the amount of Mg, as diopside is not usually abundant and Mg is also derived from the breakdown of olivine as well as pyroxenes. The generally higher Mg than Ca contents in the present samples agree with this.

Although it could be postulated that the Ca came from the calcite marbles in the succession, this seems most unlikely, as they show no evidence of instability. Calcite marbles are common in the Connemara Schist and are not associated with calc-magnesian silicate rocks of the present type. The significant associ-



Fig. 8. Plots of al-alk against Cr, Ni, Ga, Rb and Zr ppm for the analyzed samples and published Connemara pelites (from Evans, 1964; Leake, 1958).

ation seems to be with the serpentinized ultramafics.

Sample BL3616 has 560 ppm Cr and 425 ppm Ni and has clearly been enriched in these elements as well as Mg, but has not been greatly enriched in Ca or depleted in K. This specimen is unusual in being the only analyzed sample that has been metasomatized rather strongly but without the formation of amphibole or pyroxene, the key stable mineral in this sample being phlogopite. This may have been due to insufficient Ca being available compared with the Mg. Speculatively, it is possible that the amount of Ca available might have determined the relative proportions of the pyroxene and amphibole, as diopside contains about 25% CaO but tremolite only about 11% CaO, so that tremolite would be favored if Ca was less abundant. Water deficiency seems an unlikely explanation for the presence of pyroxene.

The random arrangement of the amphibole and pyroxene in many of the rocks, and their relatively late crystallization after the F_3 folds, indicates that these minerals probably grew during a late static metamorphic phase that produced abundant andalusite and some cordierite in patches in the associated pelites. This late metamorphic phase was of lower grade than the main regional metamorphism and was characterized by considerable metasomatic movement, including substantial movement of Al and Si to give quartz-andalusite veins with much sericite and some chlorite. These veins were accompanied by massive movement of water through the metamorphic rocks. Because serpentinization is unlikely to occur above 500°C (Scarfe and Wyllie, 1967), while the co-existence of andalusite and cordierite suggests a pressure below 4 kbar (Holdaway, 1971; Bird and Fawcett, 1973), these values give maximum limits for the conditions during the metasomatic formation of the calc-magnesian silicate rocks.

Although the occurrence of the serpentinites in lenses and pods means that the metasomatized rocks could be, in the third dimension, even closer spatially to serpentine than they appear to be on the map, nevertheless it is particularly interesting that the most metasomatized rocks do not appear to envelop the serpentinites but occur in the same zone at varying distances from them. This may explain some of the numerous instances of serpentinite having apparently no metasomatic effects on the contact rocks (e.g. Turner and Verhoogen, 1960, p. 319), that has often led to the deduction that no loss of Mg or Si occurred from the serpentinite during its formation. If the optimum conditions for fixation of the removed material are not immediately adjoining the ultramafic rock, a more favored site further away may be metasomatized. This would not necessarily be apparent if the examination does not range well outside the serpentinite envelope or if calc-magnesian silicate rocks of the present type are not regarded as possibly being formed by metasomatism, a deduction only made by the present author when the chemical evidence made a simple sedimentary origin untenable.

Recent oxygen and hydrogen isotope studies have shown that much of the water involved in serpentinization and other hydrothermal processes is often heated meteoric ground water (*e.g.* Taylor and Forester, 1971; Taylor, 1977), and that serpentinization is often a near-surface effect. The present results with serpentinization occurring during the formation of andalusite, cordierite, amphibole, and pyroxene indicate a metamorphic situation with a moderate pressure. It would be extremely valuable to know if meteoric water penetrates to the depth at which these common metamorphic minerals form. According to Taylor and Forrester (1971, Fig. 5) meteoric ground waters penetrate at least 3 km in depth, equivalent to more than 1 kbar pressure.

It is extremely unlikely that the solutions carrying the Ca, Mg, and probable Si contained these elements in the proportions in which they occur in amphibole or pyroxene (even allowing for the contribution of the original composition of the rock), so that the amphibole- or pyroxene-rich calc-magnesian silicate rocks do not precisely reflect the compositions of

the solutions. The rock compositions must be the product of the interaction of the original composition (possibly with some ratios such as Ti/Al being little changed), the metasomatizing solutions, and the composition of the stable minerals in that environment: an interacting trinity. Equally interesting is the deduction that the crystallization of the amphiboles and pyroxenes was a consequence of the instability of olivine and pyroxene elsewhere and that the composition of the metasomatizing solutions was strongly influenced by this instability: a partial mineralogical control of the composition of the solutions. The pinpointing of the origin of the solutions has been facilitated by the association with particular trace elements, and this feature may occur in other situations such as when cordierite, a mineral known to concentrate Be, is pinitized. Whether the Be leaves the rock will be determined largely by whether pinite or any of the other alteration products forming at that time can accommodate Be. If not, then the intergranular fluid will carry the Be away to deposit it eventually elsewhere, perhaps in a concentrated form. Thus mineral stabilities and instabilities in metamorphism can be a partial control over the chemical composition of metamorphic rocks, whereas the reverse view has traditionally dominated, namely that the minerals in a metamorphic rock are entirely controlled by the conditions of metamorphism and the original composition of the rock.

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