Trace-element distribution in a garnet–chlorite rock from Foel Ddu, near Harlech, Merionethshire.

By P. A. Mohr, B.Sc., Ph.D.

Department of Geology, University of Manchester.

Summary.--Analytical data on a garnet–chlorite rock and the contained garnet with spectrographic determinations of the trace elements are presented, and the principles determining the distribution of these elements between the garnet and the chlorite are discussed.

THE distribution of minor elements among coexisting phases during the crystallization (or recrystallization) of a rock results from the operation of crystallochemical factors, notably the ionic radii of the elements and their electronegativities. The role of the ionic radius factor is well known from the classic work of Goldschmidt. Consideration of electronegativity is more recent. Pauling (1946) defines electronegativity as 'the power of an atom in a molecule to attract electrons to itself', in other words the tendency to covalent bonding; this implies that the electronegativities of bonded atoms influence the nature of the bond formed. The bonding in minerals is rarely purely ionic but usually has a partial covalent character in consequence of which the minor element contents do not always accord with those anticipated on the basis of pure ionic bondings. Ramberg (1952) has discussed the theoretical basis for the effect of electronegativity on element distribution between coexisting silicates; he showed that the more complex silicates (i.e. those with more Si- -O- -Si bonding) attract weakly electronegative elements more strongly. De Vore (1955) applied this principle to crystal growth; he noted that the adsorption of impurities on growing crystal faces depends on the polarizing power, in effect the electronegativity, of the adsorbed cation and the polarization of the mineral surface, which in turn depends on the polarized nature of the oxygen ions in the structure. Ringwood (1955) explored the effect of electronegativity on diadochic substitutions within a given mineral structure and during the crystallization of magmas, but little work has been done on the relative importance of ionic radius and electronegativity in controlling the distribution of minor elements

among coexisting minerals. During an investigation of the geochemistry of the rocks of the Manganese Shale group (Lower Cambrian) of the Harlech district, an opportunity arose to evaluate this for the distribution of minor elements among the minerals of a metamorphic rock. This paper presents the results.
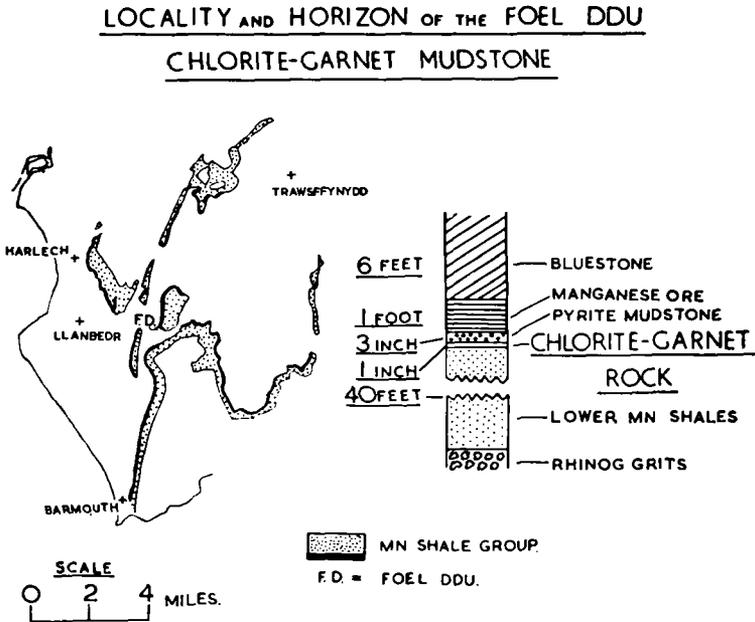

FIG. 1.

Rock description. The rock is a soft, bright green, slightly cleaved mudstone and is exposed in the wall of an old mine level on the hill Foel Ddu, ½ mile NNW. of Pont Cerig, Nanteol (fig. 1). It occurs immediately below the pyritiferous mudstone which underlies the distinctive Manganese Ore horizon (Woodland, 1939). It has not been encountered elsewhere in the area and was not found in the nearest adjacent exposures of the corresponding horizon in the Lower Cambrian Manganese Shale group.

It consists essentially of garnet, chlorite, and quartz. The garnets are colourless, sub- to euhedral, 0·02–0·005 mm. in diameter, and occur scattered in a matrix of laths and irregular flakes of pale green weakly

pleochroic chlorite, average size 0.025×0.005 mm., which lie subparallel to the bedding; a light-coloured band, 2 mm. thick, is rich in comparatively large (0.05–0.025 mm.) euhedral garnets with interstitial quartz and sparse recrystallized felspar. Visible accessory minerals in the rock include minor iron ore, rare tourmaline, and very rare flakes of white mica; carbonate minerals are absent. The chemical analysis of the rock (table I, col. 1) shows the high manganese content to be expected in a member of the Manganese Shale group. Comparison of the chemical and mineralogical data indicates the presence of considerable amounts of quartz, which is not visible in thin section and must be intimately mixed with and obscured by the chlorite; confirmation of this is obtained from the X-ray powder photograph of the chlorite fraction which contains quartz lines in addition to those of the dominant mineral.

The composition of the rock suggests that chemical precipitation played a significant part in the formation of the original sediment, which has since been completely recrystallized by low-grade dynamic metamorphism. The virtual absence of detrital minerals indicates deposition in quiet waters. The absence of carbonates may indicate precipitation in an environment of pH slightly below 7 and medium oxidation potential (Huber and Garrels, 1953; James, 1954), probably from waters carrying colloidal suspensions of silica, clay minerals, and possibly iron hydroxide, and solutions of iron, manganese, magnesium, and calcium as bicarbonates.

The chemical compositions of the garnet and chlorite have been determined only approximately, since it is not essential that they should be known accurately in a study of this nature. From such fine-grained material the separation of sufficient amounts of the pure minerals for complete chemical analyses would involve much tedious purification, and it is doubtful whether the results would justify the labour involved, particularly in view of the intimate mixing of the chlorite and quartz. Nevertheless the composition of each mineral was estimated in two ways, with fair to good agreement between them in both cases.

The garnet was separated from the rock by centrifuging the finely crushed specimen in methylene iodide. A small quantity of garnet of 99.5 % purity was obtained, from which the small amount of iron ore impurity was extracted with a magnet. On the purified sample MnO was determined colorimetrically to be 21.10 ± 0.35 %.[1] Taken in

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[1] The colorimetric method was preferred despite the magnitude of the error since experience of the gravimetric method had confirmed its reputed unsatisfactory nature.

conjunction with the refractive index, $n = 1 \cdot 823 \pm 0 \cdot 002$, this indicates a composition: spessartine 49 %, almandine 36 %, andradite 15 % (using the diagram of Winchell (1951) for the pyralspite-andradite system). Wright (1938) showed that garnets rarely contain important quantities of more than three end-member molecules, so that the content of grossular and pyrope in the Foel Ddu garnet is unlikely to exceed 5 %.

Confirmation of the composition quoted is afforded by a consideration of the CaO content of the rock. Assuming that all the calcium is in the garnet (since this element does not normally enter either chlorite or quartz) and using the estimate[1] that this mineral makes 20 % by weight of the rock, the garnet should contain 16 % of the andradite molecule. This value is in good agreement with that deduced above. The unit-cell dimension, $a = 11 \cdot 617 \pm 0 \cdot 003$ Å., confirms the presence of Ca in the garnet. Using the data of Stockwell (1927) and Fleischer (1937) and the above figure of 16 % andradite, the garnet composition may be calculated to lie between 40 and 47 % spessartine (44 and 37 % almandine), a satisfactory confirmation of the composition quoted above. The cell dimension for a garnet of that composition may be calculated to be $a = 11 \cdot 616$ Å., i.e. within the limits of the determined value. This garnet differs considerably from that occurring in the Manganese Ore of which compositions were calculated by Woodland (1939), and resembles more closely the spessartine-almandine garnets of low-grade metamorphic pelitic rocks (Tilley, 1926).

The chlorite fraction could not be obtained sufficiently pure from quartz to justify direct chemical analysis. An approximation to its chemical composition can be obtained by subtracting 20 % by weight of garnet of the above composition from the total rock analysis, omitting TiO_2, P_2O_5, alkalis, and H_2O-, and assuming that the remainder is a mixture of quartz with an orthochlorite whose composition lies between $(Mg,Fe'')_2Al_2SiO_5(OH)_4$ and $(Mg,Fe'')_3Si_2O_5(OH)_4$. Hey (1954) suggested 4 % Fe_2O_3 as the upper limit to the Fe_2O_3 content of unoxidized orthochlorites; this value is exceeded by the recalculated Fe_2O_3 content of the present chlorite, but the excess is not important, especially since no allowance has been made for the small amount of iron ore present. So in the calculations all the iron has been recast as ferrous iron following the suggestion of Winchell (1928) that chlorites are probably all strictly

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[1] Estimate based on proportions obtained during mineral separations. Micrometric analysis gave a somewhat higher value (22 % by volume) but with a fine-grained aggregate, such as this rock, there is a tendency to overestimate the mineral of high relief.

ferrous minerals as originally formed but are liable to an oxidation of the type $Fe''OH \rightarrow Fe'''O$. From the data in table I, col. 3, atomic proportions of Si, Al, all iron as Fe'', Mg and OH were calculated; Al was divided equally between a (Si,Al) group and a (Fe''MgAl) group and the excess of the former over two-thirds of the latter was attributed to surplus Si present as quartz in the mixture; it is equivalent to 30 % quartz (to the nearest 0·5 %). Total impurities in the mixture thus amount to 33·5 %, and the chlorite composition works out as

$$(Fe_{3\cdot2}Mg_{1\cdot2}Al_{1\cdot6})(Al_{1\cdot6}Si_{2\cdot4})O_{10\cdot4}(OH)_{7\cdot6}$$

(table I, col. 4, where the distinction between Fe''' and Fe'' has been retained). These figures will not be accurate but since this study is concerned with major differences in element distribution they should be adequate. Confirmation of this composition is afforded by the optical properties of the chlorite fraction; the β refractive index was determined as $1\cdot630 \pm 0\cdot01$ and the birefringence as $0\cdot004$. Although the mixture law cannot properly be applied to aggregates it gives some indication of how these figures should be corrected for the presence of 30 % quartz intimately associated with the chlorite. The expression

$$100 \times 1\cdot630 = 70n + 30 \times 1\cdot547$$

yields a value of $n = 1\cdot666$ and indicates that the true β refractive index of the chlorite is nearer $1\cdot66$. From the diagram of Hey (1954) the optical properties of a chlorite of the calculated composition are refractive index $1\cdot658$, birefringence $0\cdot002$, in satisfactory agreement with the figures deduced above.

Minor elements in the rock, garnet, and chlorite. The minor elements were determined spectrographically and the results are shown in table I. Internal standardization methods were used with Pd as internal standard for Co, Ni, Cr, V, Cu, Mo, and Zr, and with Ca for Sr and Ba. The other elements listed were determined by visual comparison with standard spectrograms. The sample was mixed with two parts by weight of carbon and appropriate amounts of Pd and Ca (10,000 p.p.m. Pd as $(NH_4)_2PdCl_4$; 1 part by weight $CaCO_3$) and arced to completion in a D.C. arc using anode excitation. The probable errors are: Sr, Ba ± 4 % ; Co, Ni, Cr, V, Cu, Mo ± 5–7 % ; Zr ± 15 % ; Sc, Yt, Ag ± 30 %.

Both the rock (col. 1) and the garnet fraction (col. 2) were directly analysed for the minor elements. The minor element contents of the chlorite were calculated by subtracting from the amounts found in the rock the amounts contained in 20 % garnet and then making allowance

TABLE I. Chemical data on a garnet–chlorite–quartz rock from Foel Ddu, near Harlech, Merionethshire.

Major elements in wt. %.	1.	2.	3.	4.	Minor elements in parts per million.	1.	2.	3.	4.
SiO_2	43·30	36·1	45	22·5	Ba	190	11	235	358
TiO_2	0·79	—	1	—	Ag	15	80	nil	nil
Al_2O_3	17·09	17·5	17	25·5	Pb	< 30	< 30	< 30	—
Fe_2O_3	4·13	4·7	4	6	Sr	28	5	35	53
FeO	18·34	15·6	19	28·5	La	< 30	< 30	< 30	—
MnO	4·33	21·1*	—	—	Yt	90	350	25	38
MgO	4·21	—	5	7·5	Sc	10	30	5	8
CaO	1·07	5·0	—	—	Zr	50	250	nil	nil
Na_2O	0·67	—	1	—	Zn	< 250	< 250	< 250	—
K_2O	0·31	—	0·5	—	Co	< 2	3	< 2	< 2
P_2O_5	0·30	—	0·5	—	Cu	45	38	47	71
H_2O+	5·60	—	7	10·5	Sn	< 20	< 20	< 20	—
H_2O-	0·35	—	0·5	—	Mo	< 1	1·7	< 1	< 1
CO_2	nil	—	—	—	Ni	45	9	60	90
Total	100·49	100	100·5	100·5	Li	10	—	—	—
					V	400	54	490	735
					Cr	75	34	85	128
					Be	< 2	—	—	—

1. Garnet–chlorite–quartz rock, Foel Ddu, near Harlech, Merionethshire.
2. Calculated composition of the garnet in 1, based on the refractive index and an MnO determination. Minor elements determined spectrographically.
3. Composition of the chlorite–quartz fraction of 1, derived by subtraction of 20 % of the garnet, 2 (to nearest 0·5 %).
4. Calculated composition of the chlorite, derived from col. 3 by setting aside TiO_2, P_2O_5, alkalis, and H_2O- as non-structural and correcting for quartz contamination as indicated in the text.

* Direct determination; all other major constituents in col. 2 and the whole of cols. 3 and 4 are indirect calculations.

for the quartz and other impurities in the chlorite fraction, on the assumption that the minor elements of the quartz will be negligible compared with those of the chlorite (cols. 3, 4).

Sc and Yt have not been detected in any other rock of the Manganese Shale group. Yt, here concentrated in the garnet, has been shown to occur frequently in manganese-rich garnets (Jaffe, 1951), but it is not clear whether metamorphic segregation is solely responsible for the contents of these elements exceeding the limits of detection in this localized rock.

Distribution of the elements between the garnet and the chlorite.

The minor element contents of these two minerals represent the result of crystallochemical factors operating during the recrystallization of the rock. It is not possible to distinguish whether the chlorite or the garnet crystallized first, or whether both formed simultaneously, but the time-lapse, if any, is unlikely to have been great and a distribution equilibrium between the garnet and chlorite phases is probable.

The oxygen ions in the chlorite are more electronegative than those in the garnet on account of the increased Si—O—Si bonding in the former.

The presence of considerable Al replacing Si in the chlorite will lower the electronegativities of the oxygen ions of that mineral (compare Ramberg, 1952) but nevertheless a comparatively large difference in the polarizability of the garnet and chlorite crystal surfaces can be expected, and, in consequence, a relatively strong fractionation of the minor elements between these two minerals. The more electronegative cations should tend to be adsorbed on the less electronegative garnet surface rather than on the chlorite.

Fractionation ratios, $C/G = $ (content of minor element in the chlorite)/ (content of the same element in the garnet), have been determined for various elements. For the purposes of discussion the elements are grouped according to ionic size, and for each group an attempt made to determine how far the sequence of fractionation ratios is determined by relative ionic radii and how far by electronegativity.

Ions larger than 1·1 Å., which cannot conveniently enter either mineral structure, are adsorbed by the structure and reside in structural defects. The elements, arranged in order of decreasing electronegativity (following Fyfe, 1951) and with their ionic radii quoted in brackets, have the following fractionation ratios, C/G: Ag (1·26 Å.) very low; Sr (1·12 Å.) 11; Ba (1·34 Å.) 33.

The order of increasing fractionation ratios is that of decreasing electronegativity and appears unrelated to ionic radii, so that for elements that do not normally enter either structure electronegativity appears more important than ionic radius in determining the distribution.

Ions smaller than 1·1 Å. can enter one or both of the mineral structures. The formulae for these structures may be written: $X_3Y_2(SiO_4)_3$ and $X_{(6-a)}Y_a(Si_{4-a}Al_a)O_{10}(OH)_8$, where $X = $ Fe″, Mn″, Mg″, or Ca″, or minor elements proxying for these major ones and $Y = $ Al‴, Fe‴, or minor elements. But in the garnet structure the X group ions are in eightfold coordination whereas in the chlorite they are in sixfold. It is advisable, therefore, to subdivide this group of ions into three: those of ionic radius 0·78–1·1 Å. and thus more likely to occur in eightfold coordination, those of ionic radius 0·65–0·78 Å., and those of ionic radius 0·50–0·65 Å. and thus more likely to occur in sixfold coordination.

The fractionation ratios, C/G, of elements with ionic radii in the range 0·78–1·1 Å., arranged in order of decreasing electronegativity, are: Zr (0·79 Å.) very low; Sc (0·81 Å.) 0·27; Yt (0·92 Å.) 0·11. For Mn (0·80 Å.) and Ca (0·99 Å.) the ratios are also very low. While the less electronegative Sc has a higher fractionation ratio than Zr and Mn, both of similar dimensions, the ratio for Yt is lower and suggests that within

this group ionic radius is more important than electronegativity in determining the distribution. Only when the ionic radii are very similar does it appear that electronegativity exerts any influence on the relative distribution of the elements. The consistently low values for all the ratios in this group emphasize the tendency for ions of radii within this range to enter the eightfold coordinated positions in the garnet structure.

The fractionation ratios, C/G, of elements with ionic radii in the range 0·65–0·78 Å., arranged similarly, are: Cu (0·72 Å.) 1·87; Co (0·72 Å.) < 0·7; Ni (0·69 Å.) 10; Fe (0·74 Å.) 1·83; Mo^{4+} (0·70 Å.) < 0·6; Mg (0·66 Å.) high, probably > 15. It is apparent that the smaller ions have higher ratios while the order of increasing fractionation ratios shows little relationship to the electro-negativity sequence. Mo^{4+} and Co appear as exceptions. The case of Mo^{4+} is complicated by doubts as to its true valency and is discussed below. There is no obvious explanation for the Co anomaly but even in the garnet, the only specimen in which it was detected, its quantity was so near to the limit of detection of the method used that no great reliance can be placed on the figures obtained. If it be assumed that the Fe in the chlorite was originally all, or nearly all, in the ferrous condition the fractionation ratio for Fe″ would have to be increased; if all the iron in this mineral is recalculated as Fe″ the ratio becomes 2·17 and a slight anomaly in the sequence is introduced, which might be interpreted as a slight electronegativity effect, but in view of the uncertainty of the assumption no real significance can be attached to this feature.

The fractionation ratios, C/G, of elements with ionic radii in the range 0·50–0·65 Å., arranged in order of decreasing electronegativity, are: Mo^{6+} (0·62 Å.) < 0·6; Fe^{3+} (0·64 Å.) 1·28; V^{5+} (0·59 Å.) 13·6; Cr^{3+} (0·63 Å.) 3·76. If Mo is neglected they are in sequence with ionic radii, the smaller ions having the higher ratios.

The ratio for Mo is low, whether this element is reckoned as Mo^{4+} or Mo^{6+} and this anomaly is, as yet, unexplained. It may have arisen through the difficulties of determination, or it may indicate the presence of some complicating factor such as molybdenum occurring in different valence states in the two minerals.

In both the last two groups the fractionation ratios normally exceed unity, thus indicating the tendency for the smaller ions to enter the sixfold coordinated positions in the chlorite. It is clear that for those elements of ionic radius such that they can enter either or both of a pair of mineral structures ionic radius is a more powerful influence than electronegativity on the relative proportions of an element entering the

two structures. Only when the ionic radii are very similar is the relative distribution of elements between the structures influenced by electronegativity.

Conclusions. From the above data it may be concluded that electronegativity is more important than ionic radius in determining the relative fractionation ratios of those elements that cannot be conveniently accommodated in either of a pair of mineral structures and are adsorbed, or accommodated at lattice defects. It is less important for those elements that can enter structural positions in either or both of the minerals and only exerts a detectable influence when two elements of very similar ionic radii are compared.

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