THE STRUCTURE OF THE HOST MINERAL AS DETERMINING FACTOR IN ACCOMODATION OF TRACE ELEMENTS

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ABSTRACT

A discussion of the current distribution rules of elements in rocks and minerals is given here. The criticism of the rules and the continuous trials of different authors to improve them is presented as well. Such discussion revealed the general dissatisfaction of the GOLDSCHMIDT-rules.

The authors found from their experience that the factor of the structure of the host mineral is very important in the fate of an element during magmatic crystallization. We recommend the following rule to be added to the existing rules for the distribution of elements: "The structrure of the host mineral is one of the determining factors in the allowance of elements into minerals". Various evidences from the analyses of coexisting mineral pairs are discussed in order to support this conclusion.

INTRODUCTION

The search for rules governing the distribution of elements in rocks and minerals is going on since GOLDSCHMIDT [1937]. The subject is still far from being settled and as a matter of fact much work is needed in this field. The present work exposes the old rules of GOLDSCHMIDT and RINGWOOD followed by criticizm of these rules in order to reveal their general dissatisfaction and at the same time presents the continuous trials of different authors to formulate new rules or to improve the old ones.

The present authors found from their experience with the analytical chemistry of rocks and minerals that the factor of the structure of the host mineral is an important criterion in the fate of an element during magmatic crystallization. Evidence on the importance of the structure of a crystal in allowing elements to enter will be given. The evidence includes six examples from the analytical chemistry of coexisting mineral pairs partly taken from the first authors own work or from the available literature. The following rule should be added to the existing rules for the distribution of elements: *"The structure of the host mineral is one of the determining factors in the admission of elements into minerals".*

THE GOLDSCHMIDT- AND RINGWOOD-RULES

The accomodation of an element into the crystal structure in a multicomponent system according to GOLDSCHMIDT [1937] is governed by the following rules:

1) If two ions have the same radius and the same charge, they will enter a given crystal lattice with equal facility.

2) If two ions have similar radii and the same charge, the smaller ion will enter a given crystal lattice more readily.

3) If two ions have similar radii and different charges, the ion with the higher charge will enter a given crystal lattice more readily.

Despite that GOLDSCHMIDT's rules are a significant tool toward the explanation of the distribution of the different elements during the sequence of magmatic crystallization, yet they are not completely valid and are seriously criticized [MASON, 1964]. The GOLDSCHMIDT-rules ignored the bonding character of minerals and this was considered by RINGWOOD [1955] who showed that the electronegativity of an element is a measure of its tendency to form covalent bonds and hence has an important influence on the extent to which it will replace another element of similar size.

CRITICISM AND AMENDMENT OF THE DISTRIBUTION RULES

By careful examination of subsequent literature, it is important to conclude that some modifications of GOLDSCHMIDT-rules have very important influence on interpretations of trace element geochemistry [MASON, 1964; TAYLOR, 1964]. However, the GOLDSCHMIDT-rules have again been found to lack generality, particularly with regard to the transition metal ions, with the result that dissatisfaction has been expressed, over the utility of the "rules" for accounting for element distribution [FYFE, 1964; NASSAU, 1964].

Some writers have abandoned the GOLDSCHMIDT-rules and have endeavoured to interpret trace element geochemistry by adsorption phenomena, kinetics of crystal growth and disequilibrium processes. Some aspects of transition metal geochemistry have been interpreted by crystal field theory. Other writers have formulated new rules using bond energy criteria. Adherents to the rules have proposed complex explanation for anomalous cases. As a result considerable confusion has developed in the geological literature over the nature of chemical bonding in geologic media and in minerals [BURNS and FYFE, 1967].

KRAUSKOPF [1967] mentioned that the GOLDSCHMIDT-rules of substitution give some insight into the distribution of elements in igneous rocks but leave many distinct anomalies unexplained. These anomalies can be grouped on the basis of bond character and differences in differentiation trends. KRAUSKOPF *(op. cit.)* adds that two further reasons for deviation from the rules are the tendency of some trace elements to form very stable minerals of their own and the preference of some trace elements for certain silicate structures rather than others.

BURNS and FYFE [1967] evaluated various criteria which have been used to interpret trace element geochemistry and chemical bonding in minerals. They concluded that in all cases single rules fail in simple cases and they suggested that attention must be focussed on the thermodynamic parameters governing the free energy of distribution on differences in two states, and not the parameters of any single state.

JIYAMA and VOLFINGER [1976] assumed that a foreign atom fixed in a crystal causes local lattice deformation, the deformed zone does not prohibit foreign atoms, but that the number of foreign atoms acceptable in this region depends on the total numbers of foreign atoms already fixed in the crystal.

EVIDENCE ON THE IMPORTANCE OF THE STRUCTURE
OF THE HOST MINERAL

Six evidences from the analyses of coexisting mineral pairs are given here to illustrate the preference of certain elements toward specific mineral phases:

1) *The spessartine-plagioclase feldspar pair;* KHALIL and EL SOKKARY [1971] during a study on an yttrian spessartine from a pegmatite in the South Eastern Desert of Egypt mentioned that the partition coefficient Y-garnet/Y-feldspar = 74, which reflects great preference of Y toward the Mn-bearing garnet rather than toward the Ca-bearing plagioclase. The authors were of the opinion that the geochemical relation between Y and Mn is not quite clear and worth more detailed investigation. Accordingly it is obvious that Y prefers the cubic spessartine structure which carries Mn and Fe more than the coexisting triclinic oligoclase which is a Ca-bearing feldspar. This is an example of the deviation from the strict GOLDSCHMIDT-rules.

Such rules predict that the trivalent Y^{3+} ion (r = 0.93 Å) would replace the divalent Ca^{2+} ion (r = 0.99 Å) in the plagioclase structure more readily than substituting divalent Mn^{2+} (r = 0.80 Å) or divalent iron Fe^{2+} (r = 0.76 Å) in the cubic garnet structure.

2) *The fluorite-calcite pair;* Table 1 gives the analyses of some trace elements in fluorite and coexisting calcite lying as a vein in an amphibolite body present in the central Eastern Desert of Egypt [EL SOKKARY and ABDEL MONEM, 1980].

TABLE 1

*Analyses of some trace elements (ppm) in fluorite and
calcite from the Central Eastern Desert of Egypt*

Element	Fluorite	Calcite	D (C/F)*
La	11	68	6.2
Ce	10	107	10.7
Nd	7	69	9.9
Y	89	111	1.2
Zr	10	9	0.9
Nb	12	12	1.0

* D (C/F = Distribution factor which is simply taken as the concentration of an element in calcite divided by the concentration of the same element in fluorite.

Table 1 shows clearly that the elements La, Ce and Nd are enriched in the trigonal calcite more than in the cubic coexisting fluorite lattice. Yet both calcite and fluorite are Ca-bearing minerals in which Ca is a major constituent. The enrichment factor of the three mentioned elements in calcite ranges between 6 to 11. However, with respect to the other three elements Y, Zr and Nb they are almost equally distributed between calcite and fluorite, their distribution factor ranges between 0.9 to 1.2. Thus certain rare earth elements prefer the trigonal calcium carbonate structure.

3) *The barite-calcite pair;* SALEEB RAUFAIEL et al. [1976] on the study of the barite-fluorite-calcite mineralization at Hammash, Egypt presented some analyses for barite and the coexisting calcite (Table 2).

Some trace elements (ppm) in barite and coexisting calcite from Hammash, Egypt

Element	Barite[1]	Calcite[2]	D (B/C)
Sr	8090 8275 Av. = 7715 7020	1970 2750 Av. = 2360	3.3
Li	13 22 Av. = 16 13	34 44 Av. = 39	0.4

1. Barite samples are pure
2. Samples are taken from calcite-sphalerite and calcite-barite bands

Unfortunately, the given analyses of Sr and Li are not for pure calcite samples but from calcite-sphalerite and calcite-barite mixture. The Sr of the calcite-sphalerite mixture comes mainly from calcite, while the diminutive effect of calcite on the total Sr content of the calcite-barite sample is quite clear. The lower quantity of Sr in these samples reflects the impoverishment of this element in calcite relative to barite. That Sr of calcite is in smaller quantity compared to the Sr of coexisting barite is confirmed from the statement of the authors mentioned: "the low Sr content in the lode of the calcite-barite band is due to the presence of relatively small amount of barite which is the main carrier of Sr". This assures clearly that the orthorhombic Ba sulphate mineral present as barite is more enriched in Sr than the coexisting trigonal Ca carbonate mineral which is calcite in this case. The simple distribution coefficient D(B/C) for Sr equals 3.3 tells in a numerical way that barite is enriched more than three times in Sr with respect to coexisting calcite.

The element Li is enriched in the calcitic samples, its D(B/C)=0.4. These samples are contaminated by either barite or a sulphide phase identified as sphalerite.

Analyses of pure barite samples give an average Li content of 16 ppm which is definitely lower than its value in the calcitic samples that give an average Li content of 39 ppm. Therefore the effect of barite on a barite-calcite mixture is to lower the Li content of the mix.

With respect to the effect of sulphides, GOLDSCHMIDT [1954] mentioned that Li does not occur in sulphide minerals, in sulphides of magmatic origin or in sulphides from hydrothermal solutions. The contaminating sphalerite in the calcitic material does not contribute significantly to Li. The increase in the Li content of the calcitic material comes mainly from calcite which according to Table 2 is more enriched in Li than its coexisting barite.

4) *The muscovite-potassium feldspar pair;* DE ALBUQUERQUE [1975] during a study on the partition of trace elements in coexisting muscovite and potassium feldspar of granitic rocks of Northern Portugal presented some interesting data concerning these two minerals which are reproduced in Table 3. Table 4 on the other hand gives the simple distribution coefficient for each element in the two mineral pair of the four quoted samples, beside the average distribution coefficient for each element in the four samples.

Table 4 shows that the element Ga has definite enrichment in muscovite (Av. D. = 12.49) besides the element Cs tends to show certain rising trends in muscovite (Av. D. = 1.92).

TABLE 3

Some trace elements (ppm) in muscovite and coexisting potassium feldspar in granitic rocks of Northern Portugal

Element	Muscovite (M)				K-Feldspar (F)			
	8	9	11	12	8	9	11	12
Ga	85	100	110	150	15	11	8	7
Sr	14	13	6	7	1200	800	440	160
Pb	9	5	5	—	46	65	38	23
Ba	1250	660	510	220	4750	2250	2350	1500
Rb	500	410	525	750	400	430	700	550
Cs	17	20	25	115	19	20	21	25

TABLE 4

Simple distribution factor (D) of each element in muscovite (M) and coexisting K-feldspar (F) of the granitic rocks of Northern Portugal

D	8	9	11	12	Av. D
Ga M/F	5.67	9.09	13.75	21.43	12.49
Sr M/F	0.01	0.02	0.01	0.04	0.02
Pb M/F	0.20	0.08	0.13	—	0.14
Ba M/F	0.26	0.29	0.22	0.15	0.23
Rb M/F	1.25	0.95	0.75	1.36	1.08
Cs M/F	0.89	1.00	1.19	4.60	1.92

On the other hand Rb is an element of almost equal distribution in both muscovite and the coexisting K-Feldspar (Av. D. = 1.08 and it ranges between 0.75 to 1.36). With respect to the three elements Sr, Pb and Ba, there is definite enrichment in the coexisting potassic feldspar (Av. D Sr=0.02, Av. D Pb=0.14 and Av. D Ba= =0.23). Thus Ga is surely enriched in the monoclinic phyllosilicate structure of the muscovite while Sr, Pb and Ba develop rising trends in the coexisting triclinic tectosilicate K-feldspar structure, yet both minerals are KAl-silicates.

5) *The olivine-pyroxene pair;* KRAUSKOPF [1967, p. 590] mentioned that Cr and V are generally much more concentrated in pyroxene than in coexisting olivine, while Ni and Co favour the olivine, although on the basis of ionic radii alone· the same possibility of substitution should be available in both minerals.

6) *The hornblende-biotite pair;* The partition coefficient of an element among pairs of coexisting minerals according to WEDEPOHL [1971] depends on the crystal chemical properties of the element. In coexisting amphiboles and biotites, Mn for instance prefers the amphiboles and Ni the biotite structure. WEDEPOHL continues that analyses of this type may be useful in testing the mineral assemblage of a certain rock for internal equilibrium.

CONCLUSION

The foregoing investigation shows that the structure of the host mineral which in most of the studied cases is a silicate mineral is an important factor in controlling the distribution of elements during magmatic crystallization. This is primarily based

on both experimental work on the analyses of mineral pairs as well as analyses taken from literature. It is already seen that GOLDSCHMIDT-rules have their shortcomings in interpreting the fate of minor elements during magmatic crystallization. These rules can be more useful if another factor is added to them concerning the structure of the host mineral which is necessary to explain the distribution of elements in certain cases.

A question arises here, why the structure of a mineral is a profound determining factor in acceptance of trace elements? The answer is just tentative. It may be due to the nature of the regular arrangement of the anionic groups together with the cations, it may be due to the extent of randomness of the trace element in the host structure or otherwise may be due to the fixation of the trace element either in interstitial, vacant or deformed sites of the mineral.

These substitution reactions are always interpreted on thermodynamic basis, namely the free energy change associated with change of state of the trace element say from magma into solid solution with the host.

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