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Geochemical Studies on the Role of Diadochy in the Cations Distribution in Minerals of Amphibole Group in Earth's Crust

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A series of 17 minerals belonging to amphibole group were analyzed in order to probe into the role of diadochy in their formation. All the three subgroups of amphibole are represented in these samples. Samples of each mineral have been collected from three different regions so in all 51 samples have been analyzed. All the factors controlling diadochic distribution namely ionic size, ionic charge and charge/radius ratio have been considered. Goldschmidt rules have been found to follow. Out of three parameters namely size, charge and valency, the first one seems to play pivotal role in diadochic substitutions. Stereochemical factors have also been found to influence the phenomenon significantly. The paper will enhance the understanding of formation of this important class of mineral, which have received scanty attention due to complicated crystal structures and will be useful in making new alloys.

Key Words: Diadochic study, Amphibole, Size, Charge, Valency, Stereochemistry.

INTRODUCTION

Cosmochemistry and geochemistry of elements distribution in mineral formation have attracted world wide attention[1-11]. Amphibole group of minerals have received scanty attention due to complicacies in its crystal structure and diversity in its composition. Consequently in the present program we have analyzed a group of 51 minerals obtained mainly from USA and a few from China and Canada. The mystery of this important class of mineral have been solved for the first time in detail in the present communication.

EXPERIMENTAL

The names of the minerals alongwith supplying agencies, source and places have been presented in Table-1. Mg^{2+}, SiO_2, Al^{3+}, Fe^{2+}, Ca^{2+} and Na^+ were analyzed by the usual methods as per details available in Vogel's text of quantitative inorganic analysis[12]. Mg^{2+} and Al^{3+} were examined gravimetrically by oxinate method, which were subsequently estimated volumetrically by bromate titration.

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TABLE-1
NAMES OF THE MINERALS, SUPPLYING AGENCIES WITH PLACE

S. No.	Name	Supplying agencies with place
1.	Anthrophylite	Hicks Mine, Pine Mountain, Georgia, USA
2.	Ferroanthophyllite	Shochone County, Idaho, USA
3.	Tremolite	Goldsmith Mine, North Carolina, USA
4.	Ferrotremolite	Finch Mine, Arizona, USA
5.	Edenite	Sterlin Mine, New Jersey, USA
6.	Ferro-edenite	Lincoln County, Libby, Montana, USA
7.	Richterite	Lincoln County, Libby, Montana, USA
8.	Ferro-richterite	Fountain Quarry, Pitt County, North Carolina, USA
9.	Eckermannite	Snowy Range Mine, Bolder County, North Caroline, USA
10.	Ferroeckermannite	Fountain Quarry, Pitt County, North Carolina, USA
11.	Arfvedsonite	Fountain Quarry, Pitt County, North Carolina, USA
12.	Glaucophane	Sedalia Mine, Colorado, USA
13.	Ferro-glaucophane	Wushan Spessartine Mine, Zhangzhou, Fujian, China
14.	Riebeckite	Fremont County, Colorado, USA
15.	Magnesioriebeckite	Vermiculite Mine, Fremont County, Colorado, USA
16.	Katophorite	Red Hill, Carrot County, Massachusetts, USA
17.	Magnesiokatophorite	Bealake Diggings, Tory Hill, Hliburton County, Onatario, Canada.

In the given samples, iron was present in both ferrous and ferric forms. Ferrous ion was estimated by dichromate method while for the ferric ion, reduction process was carried out to convert it into ferrous state by stannous chloride method, where excess of stannous was removed by adding mercuric chloride solution. The resultant solution was titrated against standard $K_2Cr_2O_7$ solution with the use of barium-diphenylamine sulphonate as indicator. The amount of iron was determined on the basis of calculation 1 mL of (N) $K_2Cr_2O_7$ = 0.05585 g Fe. Calcium was estimated making its known solution in aqueous medium on adding dilute HCl to it. It was converted into calcium oxalate as precipitate and subsequently dissolved in dil. H_2SO_4 which was collected into measuring flask for titration permagnometrically. 1 mL of (N) $KMNO_4$ = 0.0504 g Ca^{2+}. Other elements were estimated in a similar manner. Analytical data have been presented in Table-2.

RESULTS AND DISCUSSION

Experimental results concern amphiboles. General theories on distribution of elements have been incorporated here and the results have been discussed in that light. The discussions are mainly based on ionic substitution and diadochic replacements of the elements in the crystal lattice. Relative cation/anion radius ratio, coordination number, charge and free energy lowering are important parameters for mineral formation. Temperature, pressure and relative natural abundances are also three additional factors.

TABLE-2
ANALYTICAL DATA OF THE MINERALS OF AMPHIBOLE GROUP

Amphibole	Ions								
	Mg^{2+}			Si^{4+}			Fe^{2+} (Fe^{3+})		
	A	B	C	A	B	C	A	B	C
Anthophyllite	21.76	21.7	21.79	28.76	28.77	28.77	–	–	–
Ferroanthophyllite	–	–	–	22.44	22.42	22.44	39.03	39.03	39.03
Tremolite	14.95	14.97	14.97	27.65	27.67	27.66	–	–	–
Ferrotremolite	–	–	–	23.17	23.16	23.16	28.79	27.78	28.78
Edenite	15.05	15.05	15.05	24.36	24.35	24.35	–	–	–
Ferrodenite	–	–	–	–	–	–	29.57	29.55	29.53
Richterite	14.87	14.86	14.85	27.47	27.45	14.48	–	–	–
Ferrorickterite	–	–	–	28.05	28.00	28.01	28.59	28.62	28.62
Eckermannite	12.07	12.11	12.07	27.93	27.96	27.97	–	–	–
Ferroeckermannite	–	–	–	24.18	24.16	24.14	24.01	24.03	24.02
Arfvedsonite	–	–	–	23.41	23.43	23.45	23.27 (4.80)	23.31 (5.84)	23.31 (5.82)
Glalaucophane	9.28	9.32	9.30	28.65	28.69	28.67	–	–	–
Ferroglaucophane	–	–	–	25.60	25.61	25.53	19.09	19.07	19.08
Reibockite	–	–	–	24.00	24.00	24.00	17.93 (11.91)	17.89 (11.93)	17.88 (11.95)
Magnesioriebeckite	8.64	8.66	8.68	26.72	26.68	26.790	–	–	–
Katophorite	–	–	–	20.16	20.16	20.16	22.89 (5.74)	22.93 (5.70)	22.91 (5.72)
Ekatophorite	11.48	11.45	11.42	23.15	23.17	23.16	(6.60)	6.58)	(6.56)

Amphibole	Ions								
	Ca^{2+}			Na^{+}			Al^{3+}		
	A	B	C	A	B	C	A	B	C
Anthophyllite	–	–	–	–	–	–	–	–	–
Ferroanthophyllite	–	–	–	–	–	–	–	–	–
Tremolite	9.86	9.87	9.88	–	–	–	–	–	–
Ferrotremolite	8.27	8.26	8.26	–	–	–	–	–	–
Edenite	9.93	9.92	9.93	2.84	2.85	2.87	–	–	–
Ferrodenite	8.47	8.48	8.49	2.42	2.44	2.43	–	–	–
Richterite	4.90	4.88	4.88	5.60	5.60	5.60	–	–	–
Ferrorickterite	4.08	4.10	4.12	4.68	4.72	4.70	–	–	–
Eckermannite	–	–	–	8.54	8.60	8.57	3.34	3.36	3.35
Ferroeckermannite	–	–	–	7.38	7.42	7.43	2.88	2.92	2.90
Arfvedsonite	–	–	–	7.17	7.20	7.20	–	–	–
Glalaucophane	–	–	–	5.83	5.87	5.88	6.90	8.85	8.89
Ferroglaucophane	–	–	–	5.25	5.21	5.23	6.17	6.13	6.12
Reibockite	–	–	–	4.90	4.92	4.91	–	–	–
Magnesioriebeckite	–	–	–	4.48	4.44	4.46	–	–	–
Katophorite	4.12	4.11	4.10	4.68	4.72	4.70	2.74	2.76	2.78
Ekatophorite	4.70	4.72	4.74	5.38	5.42	5.40	3.16	3.17	3.18

A, B, C, represents three different samples of the same rock.

Elements near the surface of the earth are distributed largely between different solid phases. The first phase of development of the crust was probably the formation of a mixed molten silicate phase, with some sulphide present in solution or as dispersed silicate, sulphide and metal separated. This division is the major parting or division of minerals.

Elements which are more electropositive than iron in the series occur largely in the silicate phase, while elements which are less electropositive occur largely in the sulphide or in the metallic phase.

During the crystallization of the different phases there must have been further segregation of the elements. Thus, a fraction of the major constituents Fe, Al, Ca, Na, Mg and K was largely based on the ease of isomorphous replacement. Ions of approximately the same size *e.g.*, Mg^{2+}, Fe^{3+}, Al^{3+} and Si^{4+} can readily be taken into the same lattice site in a silicate. Larger ions are taken up either in different structures or different lattice sites of the same structures, *e.g.*, such ions as Ca^{2+}, Na^{+} and K^{+}.

It is possible that fractionation did not only occur in melts but also in the cooling of aqueous silicate solutions.

In general weathering selectively extracts the more basic ions, Na^{+}, Ca^{2+}, Fe^{2+}, Mg^{2+} and leaves the more acidic (insoluble oxides) in the rock *e.g.*, Ti^{4+}, Fe^{3+} and Al^{3+} silicates.

In considering the nature of the distribution of elements in the igneous rock minerals it is first necessary to consider the factors controlling their diadochic distribution. For this purpose Goldschimidt formulated more specific rules.

(i) For two ions to be able to replace each other in a crystal structure their ionic radii should not differ by more than 15 %.

(ii) When two ions having the same charge but different radii compete for a lattice site, the ion with the smaller radii is preferably incorporated in the lattice.

(iii) When two ions having similar radii but different charges compete for a lattice site the ion with the higher charge is preferably incorporated in the lattice.

Any ion in the structure may be replaced by another ion of similar radius without causing any serious distortion of the structure. Since minerals usually crystallize from solutions containing many ions other than those essential to the mineral, they often incorporate some foreign ions in the structure. In atomic substitution it is the size of the atoms or ions that is the governing factor and it is not essential that the substituting ions have the same charge or valency provided that electrical neutrality is maintained. Thus in passing from albite ($NaAl_2Si_3O_8$) to anorthite ($CaAl_2Si_2O_8$), Ca^{2+} substitutes for Na^{+} and electrical neutrality is maintained by the coupled substitution of Al^{3+} for Si^{4+} similarly in diopside ($CaMgSi_2O_6$) Mg^{2+}-Si^{4+} may be replaced in part by Al^{3+}-Al^{3+}. Such coupled substitutions are especially common in silicate minerals.

As a general rule, little or no atomic substitution takes place when the difference in charge on the ion is greater than one, even when size is appropriate (*e.g.*, Zr^{4+} does not substitute for Mn^{2+} nor Y^{3+} replace Na^{+}). The difficulty in balancing the charge requirements by other substitutions may be one of the reasons.

The extent to which atomic substitution takes place is determined by the nature of the structure, the closeness of corresponding ionic radii and the temperature of the formation of the substance. The nature of the structure evidently has considerable influence on the degree of atomic substitution. Some structures such as those of spinel and apatite are well known for atomic substitution whereas others such as quartz show rarity. In part this is due to the lack of foreign ions of suitable size.

The consequence of atomic substitution is that most minerals contain not only the elements characteristics of the particular species but also other elements able to fit into the crystal lattice. For instance, dolomite is theoretically a simple carbonate of Mg and Ca, but dolomites are found whose analysis show a considerable content of Fe and Mn. It is more illuminating as well as correct to consider them as products of the diadochic substitution of Fe and Mn. Furthermore, many examples show substantial deviations from Goldschmidt's rules for interchanging ions.

The most typical example of such deviations is the diadochic substitution of silicon and magnesium by aluminium. For the substitution of a silicon occurring in tetrahedral environment the difference in the ionic radii of Al^{3+} and Si^{4+} is 46 % (Al^{3+} = 0.57 Å, Si^{4+} = 0.39 Å) for this particular pair of the difference is considerably smaller if other radii are used, namely Al^{3+} = 0.51 Å and Si^{4+} = 0.42 Å), when Al^{3+} replaces Mg^{2+} present in six coordinates, the difference in the radii of Al^{3+} and Mg^{2+} is 37 %. It must be pointed out, however, that in the first case there occurs a simultaneous interchanging of Ca and Na whose ionic radii differ by only 8 % and in the second case a Mg atom is replaced by lithium which has the same ionic radius as Mg. Difference in ionic radii which exceed the specified 15 % may also arise from other causes. Sobalov, in particular paid special attention to the temperature factor. Taking the effect of the factor into account he even considered it possible to modify the formation of Goldschmidt rule somewhat by proposing that for the same valency and same type of ion the ability of ions to replace one another in a crystal lattice decreases with an increase in the difference between the ionic radii. It is assumed that for difference of 15-40 % between the ionic radii, continuous series of mixed crystals may still be formed from melts but on lowering the temperature there may occur a partial breakdown of the solid solutions and a decrease in the limit of solubility. In considering the mechanism of diadochy Goldschimdt based his rules on the energy gains or losses of substitution. This even found reflection in his terminology, ions with a higher charge, 'captured' by the lattice and ions with a lower charge only being 'admited' into the lattice. In recent years, the energy aspects of diadochy and the energy properties of the elements have received a fairly large amount of attention but it seems that the limits of the fields of application of these methods of investigation must be fairly clearly defined. There is no doubt that they are fully applicable to the studies of diadochic mixture in which competiting components are present in comparable quantities. With respect to such compounds it must be noted that Goldschimdt approach by estimating the energy gains in heterovalent substitution is not entirely correct. An elementary energy calculation of the diadochic substitution of Ca^{2+}, Al^{3+} by Na^{+}, Si^{4+} shows that such process has a gain in energy inspite of the fact that Na^{+} should only be admitted into the lattice of a basic plagioclase according to Goldschimdt's rule and terminology.

A quantitative study of the distribution of ore elements in rock minerals has shown that apparently no less important part than diadochic form of occurrence is played in rocks by forms of atomic and molecular dispersion of these elements which are formed from the decomposition of solid solutions or by absorptive capture and also by microscopic and sub-microscopic deposits of the corresponding ore minerals.

In recent years the problem of geochemistry of the trace elements in igneous rocks has become predominant.

The interest in the problem is not casual for the study of the mechanism in the distribution of the trace elements during the crystallization and differentiation of magmas but is of substantial importance for solving many problems in the theory of ore formation.

The study of the geochemistry of the trace elements in igneous rocks first provides a possibility of approaching a solution to the problems of the sources of ore material for the hypogenic ore deposits and of developing objective geochemical criteria for the genetic relationship between intrusions and mineralization. Furthermore a systematic quantitative study of the features in the migration of the trace elements and particularly the ore elements during various post magmatic changes in rocks is extremely important for the correct solution to many problems of the theory of ore formation.

A number of important problems in petrogenesis may be solved by using data on the nature of the distribution of the trace elements in igneous rocks. These data can first of all in the analysis of igneous rock complexes in geochemical surveying and also in determining the age sequence of intrusions by individual intrusive phases. The problem of the geochemistry of trace elements in igneous rocks should be considered from two aspects. On the one hand it is necessary to establish rules for this distribution during the crystallization of molten magmas. This mainly consists of studying the variations in this distribution in rock minerals and the form in which these elements occur in the rocks studied. The second aspects of the problem is to determine the features of the geochemical history of the trace elements during the differentiation of magmas of varying composition. This being solved mainly by studying the prevalence of these elements in genetically associated series of rocks. Until recently the features of the distribution of the trace elements in rock minerals have been considered from the point of view of diadochy. In the initial stages of the development of the problem of the trace elements the concept of the dominating significance of diadochy enabled important features of their behaviour under condition of the earth's crust to be established and the similarity in behaviour of whole groups of elements during various processes to be found. From the quantitative study of the distribution of the traces elements in the rock minerals it was found that for some elements a diadochic form of occurrence cannot be considered as unique. It was found that all trace elements may be divided into three large groups according to the nature of the distribution of rocks.

The uptake of an ion into a crystal from melt can be thought of being characterized by fixed value for all the atoms as a degree of the interatomic distances. The two terms are consistent with a greater bond energy, lower heat content, on formation of the solid phase. An element which is particularly established in an octahedral coordination site will be expected to gain somewhat in stability (ligand field energy)[13] on passing from a melt of irregular coordination number to a regular solid which provides such an octahedral hole. It has been established that the ligand field energies of *d*-electrons are important in the stabilization of transition metal ion in certain coordination symmetries rather than in others. In an octahedral site these energies are in the order.

$$Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+}$$

$$Ni^{2+} > Cu^{2+} > Zn^{2+} \text{ and}$$

$$Si^{3+} > V^{3+} > Si^{3+} = Ga^{3+} = Fe^{3+}$$

It is concluded that selective uptake is based upon ligand field stablization energies which are highly dependent upon hole symmetry and inter atomic distance. It is worthnoting that divalent ions and trivalent ions which accumulate most readily are those with highest melting oxides. In minerals providing holes of quite other symmetry, the order of uptake will be different again.

Crystal chemistry of amphiboles: The amphiboles structure is characterized by chains or tetrahedrally coordinated cations cross linked to form paired polymers of infinite length parallel to a crystallographic axis[14]. The basic building blocks, the tetrahedra, share alternatively two and three oxygens between consecutive tetrahedrally coordinated cations in the chain. Each link of the chain consists of a six member tetrahedral ring, surrounding a central hole.

Oxygens shared by pairs of 4 fold coordinated cations are termed bridging oxygens. Packs of the chain consist of nearly coplanar oxygens, the sites conventionally are designated as the nonbridging O_4 and bridging O_5, O_6 and O_7. The latter anions are bonded to tetrahedrally coordinated cations only but O_4 is located at the periphery of the chain and is bonded to a cation of 6-8 fold coordination. Apical oxygens lie in the next, nearly coplanar anionic layers. They occupy the non-bridging O_1 and O_2 sites and are bonded on one side to a 4 fold coordinated cations, on the other to 6-5 fold coordinated cations. Also located within this anionic layer is an anionic positioned directly over the double chain hole, anions located in this site, O_3 are bonded to such cations. Accordingly the O_3 anion is typically monovalent, either OH^- or F^- except in oxidized varieties where it is O^{2-} in contrast to the divalent oxygens which occupy all other anionic sites.

Cation structural sites consist of the following: the tetrahedrally coordinated Si_I and Si_{II}, octahedrally coordinated M_1, M_2 and M_3 6-8 fold coordinated M_4 and are approximately 10-12 fold coordinated site which may or may not be occupied. Si_I and Si_{II} cations are located in tetrahedral interstices between the oxygen layer which constitutes the back of double chain and the typical oxygen layer.

The M position are situated between two layers of apical oxygens M_2 and M_4 located at the margins of adjacent opposite facing chains provide the attractive force which bind the chains together parallel to the a and b crystallographic axes. M_2 and M_4 sites correspond to 6-8 coordination position and M_1 and M_3 sites correspond to 6-8 coordination position. The M_1 and M_3 sites located well within the cations layer and flanked on both sides by apical oxygen layers are equivalent to octahedral cations sites.

Amphiboles[4] may be described adequately by the structural formula W_0 X_2 Y_5 Z_8 O_{22} (OH, O, F$)_2$ which represents the one half of the cations in the unit cell, W represents 10-12 fold coordinated cations occupying the structural site, X stands for six or eight fold coordinated cations positioned in M_4, Y indicates 6-fold coordinated cations in M_1, M_2 and M_3 and Z refers to tetrahedrally coordinated cations in Si_I and Si_{II}.

Anions are almost invariably oxygen in the O_1, O_2, O_4, O_5, O_6 and O_7 positions. The site generally contains monovalent OH (or F) as necessitated by the condition that this anion is not bonded to 2 cations of the tetrahedral chains. In amphiboles hydrogen deficiency may arise through replacement of OH by O, with concomitant substitution of a cation by a species of higher positive charge, hydrogen excess might occur either through proton fixation by oxygens in addition to those residing in O_3 or by the presence of H_3O^+ in the position. Variation in proportion of the anions is extremely limited compared to cations substitution and hence compositional range in the amphiboles is usually discussed in terms of cations only.

Classification: The amphiboles may be divided conveniently into three groups based on the identity of X cation that is principal occupant of the M_4 site. These three groups are: iron-magnesium amphibole, calcic amphiboles and sodic amphiboles.

Iron magnesium amphiboles: Members of the cummingtonite grumerite and anthophylite-ferroanthophyllite series are chemically the simplest amphiboles. These are adequately represented by the formula $(Mg, Fe^{2+})_2$ $(Mg, Fe^{2+})_5Si_8O_{22}(OH, O, P)_2$, however, orthorhombic aluminous varieties, collectively termed the gerdites, are also fairly common. Chemical variation among the orthorhombic amphiboles is essentially continuous from anthophyllite to both gedrite and ferrogedrite. Monoclinic amphiboles range from fairly near cummingtonite to the $Fe_7^{2+}Si_8O_{22}(OH)_2$ and member granite although slightly aluminous varieties are not rare.

The rarity of ferrous iron-rich natural amphiboles stems from three causes: (i) Fe^{2+} amphiboles have lower thermal estability limits than Mg analogous, even under the most favourable redox conditions. (ii) Fe rocks which recrystallized at low temperatures also recrystallized at relatively low oxygen concentration where ferrous amphiboles are stable. (iii) Equilibrium element participating between a coexisting amphibole and more refractory silicates generally enriched the amphibole in Mg relative to Fe^{2+}.

Calcic amphiboles: The calcic amphiboles edenite, tremolite, tschermakite and the hornblendes magmesiochastingsite, pargasite and iron-bearing equivalents are members of complicated solid solution series. This is reflected in their variable chemical compositions $(Na, K)_{0-1}$, $(Na, Ca, Mn^{2+}, Mg, Fe^{2+})_2$, $(Mg, Fe^{2+}, F^{3+}, Mn^{2+}, Ti, Al)_5$ $(Si, Al, Fe^{3+})_8$ O_{22} $(OH, O, F)_2$. Intermediate members of the tremolite-ferrotremolite series known as actinolites are referred to complex Na-Al calcic amphiboles collectively as hornblends. Hornblends have immense chemical complexity. Not only do the number of component exceed three, but the substitution of some ions can take place in dissimilar structural sites giving rise to different properties. For example, iron can be found in tetrahedral, octahedral and perhaps eight fold sites, the site Fe occupies as well as its valence state affects the physical properties of the amphibole and probably even the occupancy of other sites.

Sodic amphiboles: Sodic amphiboles are somewhat less complicated, with the exception of arfvodsonites and katophorites which contain tetrahedral aluminium, rarely minor from fold coordinated ferric iron and alkali metal from iron in the Å site, most sodic amphiboles can be referred to the galucophane and magnesioribeckite series with the formula $(Na, K, Ca)_2$ $(Mg, Fe^{2+}, Fe^{3+}, Al)_5$ Si_8 O_{22} $(OH, O, F)_2$. Sodic amphiboles are less common than calcic analogues but chemical variation is virtually complete among the three members galucophane, magnesio riebeckite termed crossties. Amphiboles closely approaching the composition of ferroglaucophane apparently do not occur in nature.

Sodic amphiboles are less abundant than calcic amphiboles because either per alkaline chemical conditions or relatively high pressure and low temperature are required for their formations.

Diadochic substitution: Alkali metals do not form any simple compounds in igneous rocks. They are present only in complex compounds formed together with other metals. This fact is caused by the high solubility of this simple salts. Sodium and potassium occur only as univalent cations with radii 0.98 and 1.63 Å, respectively. Consequently they require considerable space in mineral structures. The coordination numbers of these cations are therefore, necessarily high and the interatomic forces binding sodium and potassium in mineral structure cannot be very strong.

In alkalc rocks potassium and sodium are present both in feldspars and in feldspathoids. They are also found as constituents of the alkali pyroxenes and alkali amphiboles and a number of complex titanium and zirconium silicates but the geochemical significance of those minerals is small. Sodium is the more important of these alkali metals in the alkali amphiboles and pyroxenes. It is incorporated in these minerals if there is a definite excess of sodium over aluminium. The large ionic radius of potassium prevents the incorporation of notable amounts of this metal in the amphibole structures.

Unlike the alkali, magnesium is able to build both simple and complex inorganic compounds which are stable under the conditions met in nature. Basic particularly, ultrabasic rocks form the proper surroundings of magnesium in the upper lithosphere.

The average composition for the various rocks of the calc-alkaliic differentiation series show that magnesium is strongly enriched in the silicate minerals which separate from the magma during early stages of crystallization.

The manner of occurrence of magnesium in igneous rocks is consequently characterized by diadochy Mg^{2+}-Fe^{2+}, the natural explanation of which is the equal size of the two ions. The diadochy is complete in nearly all mineral groups of getrological importance. As a general rule magnesium and iron become enriched in rock-making minerals when there crystallization temperature are relatively high. The melting temperatures of the silicate minerals of magnesium, lie rather high and are well in excess of those of the corresponding ferrous minerals. It is evident that Mg^{2+} ion is strongly bound within the structures *i.e.*, its energy of migration is high. Radius of Mg^{2+} ion is not very far from the optimum value required by the 6-coordination. The Mg^{2+} ion has just the proper size to fill out completely the space between six oxygen ions in contact with one another, without pushing than apart. Consequently strong bond is generated between magnesium and the oxygen ions. In case of Fe^{2+}, which is greater than Mg^{2+}, the bond is weakened, with a resulting decrease in the melting temperature of the silicates in question. Thus iron becomes concentrated in the mother liquor.

Diadochy between two ions of similar charge is best illustrated by the pair Mg^{2+}-Fe^{2+}. The diadochy of these ions plays an important role in almost all ferromagnesium minerals of rocks. Ferrous iron and magnesium replace each other in all proportions.

In diadochic substitution in which the charges are not similar, the electrostatic neutrality will be disturbed and consequently the balance must be re-established. This happens in many ways *e.g.*, through simultaneous substitution of another ion in structure.

The behaviour of calcium during normal magmatic differenatiation is somewhat different from magnesium. The early magmatic segregations which consist chiefly of Mg-rich olivine tenstatite, carry practically no calcium which remains in the residual melt. Depending on the decomposition of the melt, calcium sometimes becomes separated during the earliest stage of crystallization in calcic plagioclase. Anorthosites are thereby formed. Starting with the beginning of the main stage of crystallization, much calcium becomes incorporated in the structures of minerals which crystallize from all types of magmas. The content of calcium attains a maximum during the initial steps of the main stage and decreases regularly towards the end of differentiation.

The relatively early separation of calcium during differentiation is caused by the fact that anorthite becomes stable at a higher temperature than albite. It must be emphasized that during the crystallization, calcium is always separated in the form of the aluminosilicate plagioclase. Whereas the corresponding calcium aluminium silicate grossularite, never forms during the crystallization.

Clarke's calculations show that the pyroxenes and the amphiboles are the most important ferric constituents of igneous rocks. Referring to the average calcium content of pyroxenes and amphiboles of didochic rocks and to the average calcium content of igneous rocks, it may be calculated that approximately one half of the total amount of calcium found in igneous rocks is present in the ferric constituents and that the other half is contained in the salicic constituents. The conclusion follows that calcium is incorporated in tectosilicates are readily as in the silicates with chain and ladder structures. The phyllosillicate structure of the micas, on the other hand, is rather uninviting to calcium a conclusion derived from the variety of calcium micas.

Hence, calcium is one of the principal cations in the main constituents of igneous rocks. In addition it is an important constituent in many accessory minerals *e.g.* in apatite, sphene and fluorite. Apatite and sphene are among the first minerals to crytallize during the formation of igneous rocks, whereas fluorite regularly crystallizes last and fills the interstices between the earlier rocks.

Aluminium is the most abundant metal found in igneous rocks. Of all the elements only oxygen and silicon are more abundant than aluminium. The atomic number of aluminium is odd ($Z = 13$) and consequently this metal, according to Harkin's rule, should be less abundant than its neighbours, magnesium and silicon. But this is not the case in igneous rocks and consequently aluminium is strongly concentrated in the upper lithosphere. The abundance values show that aluminium like the alkali metals and the alkaline earth metals, is a thoroughly lithophile element. Due to this aluminium is practically absent in deeper lying geochemical shells of the earth. It is almost quantitatively concentrated in the lithosphere, the highest content being found in the uppermost parts *i.e.*, in the real crust. In the upper lithosphere aluminium is pronouncedly oxyphile element. It is always combined with oxygen, no sulphide minerals of aluminium are known to exist.

The tendency of aluminium to become concentrated in the uppermost lithosphere is reflected also by its behaviour during magmatic differentiation. Noteworthy, quantities of aluminium are not present in the early products of crystallization. In the early crystallites, aluminium occurs as an essential constituent only in plagiclase feldapars of anorthosites and in the spinels. The spinels were previously interpreted as aluminates, in which aluminium might has been replaced by ferric ion and chromium, but X-ray diffraction studies reveal their character as double oxides, containing either Al_2O_3, Fe_2O_3 or Cr_2O_3 as one of the component oxides. However, the spinels are quantitatively insignificant as rock making minerals and therefore, their importance in geochemistry of aluminium is very small. Even in the hornblendites, which no longer can be included among the early crystallites the content of aluminium is considerably lower than in the rocks separated during the main stage of crystallization. In this stage aluminium is somewhat enriched in the first rocks to crystallize, but with progressive diffrerentiation its content decreases.

The feldspars, which are quantitatively the most important constituents of igneous rocks, are aluminosilicates of certain univalent and bivalent metals. Therefore, they carry the bulk of the lithospheric aluminium. Although some trivalent metals theoretically may replace aluminium in the feldspar structure, the degree of such substitution in the feldspars is too insignificant to be of much geochemical importance.

Anorthite contains double as much aluminium as do albite and the potash feldspars. Consequently, in basic igneous rocks the plagioclase feldspars, which always are relatively rich in the anorthite component, contain more aluminium than do the albite rich plagioclases and the potash feldspar of acidic rocks. This is the reason that why aluminium is enriched in the early products of the main stage of magmatic differentiation.

In the alkalic series the syenites and nepheline, syenites cotain more aluminium than do the calc-alkalic rocks with a corresponding silica content. This is due to the presence of abundant sodic feldspar and feldspathoids among their major constituent minerals, nepheline, leucite and their major constituent minerals, nepheline, leucite and cancrinite contain more aluminium than potash feldspar does.

Along with the feldspar, the micas contain aluminium as one of the major constuents. Geochemically, biotite is the most important member of the mica group, muscovite is somewhat less important. The different biotite varieties carry from 10 to 20 % Al_2O_3. This content is of the same order of magnitude as the average alumina content of igneous rocks, calculated by Clarke and Washington[15]. Muscovite and allied micas, on the other hand, contain considerably more alumina, sometimes in excess of 30 %. Muscovite is an essential constituent almost only in granitic rocks and is nearly always absent in the more basic rocks. Biotite crystallizes prior to muscovite and may therefore become separated from water-rich magmas at a comparatively early stage. Therefore, the presence or absence of biotite does not notably affect the alumina content of igneous rocks, whereas, if muscovite is present, the aluminium content will somewhat increase in rocks crystallized toward the end of the main stage of differentiation. However, the effect of muscovite is less pronounced than that of the feldspars. Moreover, in granites the bulk of muscovite, if not all, is of secondary origin, being product of the alteration of the feldspars.

The pyroxenes and amphiboles, particularly augite and hornblende, which are the most important members of these mineral groups, are regularly aluminium bearing. However, their aluminium content is lower than aluminium content of the rock as a whole or, at most, of approximately equal magnitude.

The forgoing discussion shows that aluminium is not present in igneous rocks as a simple silicate. It is always combined with other metal to form complex aluminosilicates. X-ray diffraction studies have revealed two entirely different manners of occurrence of aluminium in silicate minerals.

All silicate mineral consists of a framework of [SiO_4] tetrahedra which are combined in various ways in the different mineral groups and form regular structure.

In the [SiO_4] tetrahedra, a part of Si^{4+} may be replaced by Al^{3+}. Owing to the great difference between the sizes of these ions, their radii being 0.39 and 0.57 Å respectively, the substitution is never complete. Its degree depends, in addition on the structural type of the mineral in questions. In the feldspars all aluminium present replace silicon in the Si-O tetetrahedra and only the ions, K^+, Na^+, Ca^{2+}, *etc*., form the cation network. In like manner Al^{3+}, partly replace Si^{4+} in the amphiboles *i.e.*, pyroxene and micas. In the amphiboles, only one third of the Si^{4+} ions may be replaced by Al^{3+}. In these minerals aluminium is also found outside the silicon-oxygen framework, occupying a position similar to that held by Mg^{2+} and Fe^{2+}. In spite of its somewhat smaller size aluminium in this case replaces Mg^{2+} and Fe^{2+} diadochically. It occurs like these ions, between the oxygen ions located in the corner of [SiO_4] tetrahedral. The coordination number of aluminium is 6. The Fe^{3+} ions have a similar manner of occurrence. In other important groups of silicate minerals aluminium also occupies two different structural positions.

In ferroeckermannite Fe^{3+} is replaced by Al^{3+}. Here Al^{3+} finds place out side the silicon oxygen framework. Whereas in magnesikatrophorite and in katophorite. Al^{3+} is part of silicon oxygen framework. Whereas in magnesikatrophorite and ferro glaucophane. Al^{3+} ion is part of Si-O framework. But in arfredyonite four ions of Fe^{2+} are replaced by four ion of Mg^{2+} while one ion Fe^{3+} is replaced by one ion of Al^{3+} in eckermannite.

Iron and magnesium, among all metals, have the highest cosmic abundance. Iron is twice as abundant as magnesium but less abundant than aluminium. From geochemical point of view, iron is the most important metal along with sulphur and other elements.

Iron has high affinity for sulphur and consequently it is called chalcophile. Considerable amounts of iron are present in the lithosphere which shows the lithophile character of this metal. With reference to its terrestrial manner of occurrence iron must also be included in the group of biophile elements and in the upper lithosphere it is oxyphile.

A general comparison of the geochemical properties of the elements belonging to the ferric group shows their lithophile tendency with increasing atomic number from titanium to nickel. The last three members of the group *viz*., iron, cobalt and nickel have the most marked siderophile and chalcophile properties.

The earliest product of magmatic differentiation include oxide minerals of iron, which usually are titaniferrous and sulphide segregation which consist chiefly of the iron monosulfide, Fes. Therefore, it may be concluded that iron is the most common and the most important constituents of the early magmatic non-silicate segregations.

The highest content of iron is the outset of the main stage of the crystallization, here represented by horn-blendites with proceedings differentiation. The content of iron decreases but the decrease is not so pronounced as is that of magnesium

Although both iron and magnesium are more abundant in basic rocks than in acidic rocks, the Fe, Mg ratio changes during the differentiation and iron finally becomes enriched in regard to magnesium during the last steps of the main stages of crystallization.

It has been found that the content of ferric iron does not change much with proceeding differentiation. On the other hand, the content of ferrous iron decreases more sharply and is mainly responsible for the increase in the Fe^{3+}/Fe^{2+} ratio. The Fe^{3+} ion may be considered so immobile that it is taken up in a suitable structure under any condition. The Fe^{2+} ion becomes enriched in the melt with respect to Mg^{2+}, but this phenomenon is probably somewhat obscured by the simultaneous oxidation of ferrous iron. In spite of the oxidation, the content of Mg^{2+} decreases much more rapidly than does the content of Fe^{2+} and therefore in an environment in which the oxidation of Fe^{2+} cannot take place, the residual liquor will be rich in iron. The ferric iron produced during the differentiation is partly incorporated in silicate structures and partly in magnetite. The content of ferrous iron is always high enough to prevent the formation of hematite.

Native iron is a rare constituents of igneous rocks and is found only in a few rocks, particularly in basalts either as a pure iron or alloyed with nickel *e.g.*, as awaruite and josephinite. The iron-bearing rock making minerals contain bi-trivalent iron. The radius of Fe^{2+} is 0.83 Å and the radius of Fe^{3+} is 0.67 Å.

Owing to the difference in their ionic sizes, ferrous and ferric iron differ with respect to their manner of occurrence in minerals structures, *i.e.*, Fe^{2+} usually accompanies Mg^{2+} (radius 0.78 Å) which it replace diadochically but Fe^{3+} usually substitutes for Al^{3+} (radius 0.57 Å). The Fe^{2+}, Mg^{2+} diadochy in mineral structure is complete and continuous, whereas the Fe^{3+}-Al^{3+} diadochy is less extensive because there is considerable difference in the sizes of these ions. The Fe^{3+}-Al^{3+} diadochy seems to occur on a more substantial scale only when aluminium occurs as a cation outside the siliconaluminum network in the aluminium silicates, not as a constituents of a complex anion, replacing silicon within the oxygen tetrahedral of the aluminosilicates.

This fact becomes evident from the comparative study of analysis of magnesioricheckite and riebeokite that ferric ion remain intact in both the species only Mg^{2+} in magnesioriebeckite is replaced by Fe^{2+} in riebeckite. Similarly, in magnesiokateorite and katophorite Fe^{3+} is not affected during differentiation, only Mg^{2+} is suitably replaced by Fe^{2+}.

Silicon oxygen are the elements most typical of the lithosphere. In the upper lithosphere as in the silicate meteorites, silicon is next to oxygen, the most abundant of all elements. The importance of silicon in the mineral kingdom is similar to that of carbon in organic compounds. In these compounds the carbon atom are linked together and usually form long chain or closed rings. Silicon is similarly able to combine with oxygen to form groups of various kinds in the structure of minerals. The basic grouping in the silicon-oxygen tetrahedron [SiO_4], the tetrahedral are combined in a number of ways to form the framework of the silicate minerals. Although silicon is the essential constituent cation in most minerals of petrological and geochemical importance. Still it occupies only a very limited space in their structures. The radius of the Si^{4+} ion is very small (0.39 Å) and therefore silicon practically disappears among the big oxygen anions in the tetrahedral.

In the lithosphere, silicon is evidently a typical oxyphile element. The average chemical composition of the most important classes of normal calc-alkalic igneous rocks show that silicon is strongly enriched toward the last phases of the main stage of crystallization. The silicon content is highest in the granites. However, petrological experiences shows that the enrichment continues still further, because there is much quartz present in granite pegmatites and its crystallization goes on through the pneumatolytic and hydrothermal stages. The quartz veins of varying grades of purity are common in igneous and metamorphic terraines. The high degree of enrichment of silicon through the differentiation is often considered measure of the progress of this phenomenon. Therefore the order of the members of a differentiation series is often based on their silica content. However, this practice is not always legitimate because there are numerous examples such as in alkalic complexes in which there is no regular change of the silica content in the differentiation series arranged according to the general geological principles established in the field. Thus two rocks the one of which is clearly the differentiation product of the other may have nearly equal silica contents. Such cases even though rather common are quantitatively important.

The enrichment of silicon in the last product of magmatic crystallization is readily understood if the crystal chemical properties of the silicate minerals are considered. The minerals containing independent [SiO_4] tetrahedra not linked by common oxygen ions usually have relatively stable structures. If the tetrahedra on the other hand share one or particularly more than one oxygen with neighbouring tetrahedra the distance between the silicon ions in question must decrease. In this case the repulsive force between the highly charged Si^{4+} ions will increase consistently with the number of the oxygen ions shared by the tetrahedra and therefore the stability of the structure will decrease. This is evidently the reason why two neighbouring [SiO_4] tetrahedra in silicates never share more than one oxygen ion. The most typical mineral in the structural group of the mesosilicates is olivine $(Mg, Fe)_2$ [SiO_4] which is also the most important constituents of the early differentiates of silicate magmas. According to its chemical composition, olivine belongs to the group of the orthosilicates which are the poorest in silica of all the silicates. The feldspars according to Clarke's (1924) calculations are the most common constituents of igneous rocks, contain the bulk of the silica found in the upper lithosphere. They are structurally tectosilicates and usually crystallize at lower temperatures than do the olivines. Likewise quartz is structurally a tectosilicates, it crystallizes at relatively low temperatures.

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