

THE ROLE AND SIGNIFICANCE OF THE COMPLEX ANIONIC POTENTIALS IN THE GEOCHEMISTRY

Part IV. Contributions to the interpretation of the Bowen's reaction series on the basis of the complex anionic potentials and the compound potentials

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1. INTRODUCTION

The separation of the colored rock-making minerals during the magmatic crystallization begins with the separation of the nesosilicates and after the crystallization of the pyroxenes and amphiboles, that is, after the crystallization of the inosilicates, the phyllosilicates separate. Thus, the succession of the colored rock-making minerals means the succession of the different structure types of silicates. At the same time, the light constituents of the *Bowen's* series belong to the same structure type (except muscovite), to the tectosilicates and during the crystallization, in this series, only the cation and, within the Si—O—Al framework, the Al : Si ratio changes.

As it is well known, the sequence is: independent SiO_4 tetrahedra — single chains — double chains — sheets, only the types of Si—O—Al networks, only the mode of the linkage of the SiO_4 tetrahedra taken into consideration.

Szádeczky-Kardoss (1954, 1955a, 1955b) dealing with the sequence of the magmatic crystallization has stated that „... the whole sequence of crystallization is simply to be taken for the sequence of decreasing compound potentials.” In Fig. 1 the values in parenthesis are the corresponding compound potentials computed by *Szádeczky-Kardoss*.

These values, however, were computed assuming the same value for the SiO_4 complex anionic potential in both the nesosilicates and tectosilicates. The author has pointed out partly that the value of the SiO_4 complex anionic potential varies depending upon the degree of polymerization of the SiO_4 tetrahedra and partly that the introduced ψ/SiO_4 potentials offer the possibility to characterize the relative stabilities of the different silicate anions too (*Grasselly*, 1958, 1959a, 1959b).

These statements probably are applicable to some extent also to the interpretation of the crystallization sequence of silicates.

2. THE ψ/SiO_4 POTENTIALS AND THE SUCCESSION OF THE STRUCTURE TYPES OF SILICATES IN THE BOWEN'S REACTION SERIES

During our considerations so far related to the SiO_4 complex anionic potentials, the change of the peculiarities of the SiO_4 tetrahedron — equally present in all the silicates of different structure types — depending on the degree of silification and expressed by the change of the numerical value of the complex anionic potential, were examined.

It may be assumed that the succession of the one-, two-, or three-dimensional Si—O—Al network in the *Bowen* series may be marked by the ψ/SiO_4 potentials. It is meant the succession of formation of the different types of Si—O—Al networks, i. e., that of the different silicate anions and not the sequence of the corresponding silicates themselves.

To look for connection between the succession of the structure types and the ψ/SiO_4 potentials seems to be expedient from the following causes:

a) the structure of the different silicates is primarily determined by the mode of the linkage of the SiO_4 tetrahedra, that is by the character of the Si—O—Al networks, however, the cations play not a negligible role.

b) The results of the infrared reflection spectroscopical examinations of silicates (*Schaefer, Matossi and Wirtz, 1934; Matossi and Krüger, 1936; Keller, Spotts and Biggs, 1952*) prove experimentally and the considerations of *Ramberg (1952, 1954)* as well as that of *Keller (1954)* based on heats of formation and bonding energies, respectively, support theoretically the fact of the change of the peculiarities of the SiO_4^{4-} complex anion (the degree of polarization of the oxygen, the character of the Si—O bond, the stability of the silicate anions) throughout the series from the nesosilicates toward the tectosilicates.

c) The change of the peculiarities of the SiO_4^{4-} anion revealing in the direction mentioned above may be marked by the variable complex anionic potentials showing a decreasing tendency from the nesosilicates toward the tectosilicates.

To interpret the succession of the formation of the different structure types determined by the character of the Si—O—Al networks an essential role may be attributed to the ψ/SiO_4 potentials. The importance of the role of the silicate anions is emphasized also by *Rankama and Sahama (1952)*: „With special reference to silicate minerals, it must be emphasized that the stability of the structure depends not only on the properties of the cations but also on the properties of the complex silicon-oxygen framework.”

The properties of the cations and complex anions may be characterized to some extent by the ionic and the complex anionic potentials, respectively, as it was pointed to also by the author dealing with the stability relations of the silicate anions (*Grasselly, 1959b*).

In the earlier computations the value of the SiO_4 complex anionic potential was 1,38 in both the nesosilicates and the tectosilicates. The succession of the single structure types actually could not be characterized by this constant value. However, pointing out the variability of this value

depending on the structure type, the concept of complex anionic potential became more meaningful. Table 1 denotes these values, taken from a previous paper of the author (*Grasselly, 1959a*).

As it can be seen from Table 1, the sequence of the decreasing ψ/SiO_4 potentials corresponds to the sequence of the structure types in the *Bowen* series, that is the decrease of the ψ/SiO_4 potentials depending upon the increase of the degree of silification is in full agreement with *Szádeczky-Kardoss's* statement that the crystallization of the minerals takes place according to the decreasing potential values.

Table 1.

Structure type	Silicate anion	Average ψ/SiO_4
Nesosilicates	SiO_4^{4-}	1,40
Sorosilicates	$\text{Si}_2\text{O}_7^{6-}$	1,22
Cyclosilicates	$\text{Si}_3\text{O}_9^{6-}$	1,05
	$\text{Si}_6\text{O}_{18}^{12-}$	
Inosilicates	single chain SiO_3^{2-}	1,05
	double chain $\text{Si}_4\text{O}_{11}^{6-}$	0,96
Phyllosilicates	$\text{Si}_2\text{O}_5^{2-}$	0,87
Tectosilicates	$\text{Al}_2\text{Si}_2\text{O}_8^{2-}$	0,80
	$\text{AlSi}_3\text{O}_8^{1-}$	0,74
	Si_4O_8^0	0,70

This series, in order of the decreasing ψ/SiO_4 values, means the succession of the formation of the different silicate anions characteristic of the different structure types and at the same time it indicates also the increasing relative stability of the silicate anions.

The above-mentioned are valid not only in the series of colored rock-making minerals but within the group of tectosilicates too, for example, in the case of crystallization sequence of calcic plagioclase-sodic plagioclase. The potential computed for $\text{Al}_2\text{Si}_2\text{O}_8^{2-}$ anion, characteristic of anorthite, is 0,80, whereas that of the $\text{AlSi}_3\text{O}_8^{1-}$, characteristic of albite, is 0,74. That is, the crystallization sequence may be characterized by the decreasing ψ/SiO_4 potentials also within the group of plagioclase feldspars.

3. REMARKS TO THE INTERPRETATION OF THE CRYSTALLIZATION SEQUENCE OF SILICATES ON THE BASIS OF COMPOUND POTENTIALS

Previously it was demonstrated that the succession of the single structure types in the *Bowen's* reaction series can be characterized by the decreasing ψ/SiO_4 potentials, because the structures of the different silicates are primarily determined by the type of the Si—O—Al network. However, taking into consideration the crystallization sequence of the different silicate compounds, the role of the cations can not be neglected.

To show that beside the complex anionic potentials also the cationic

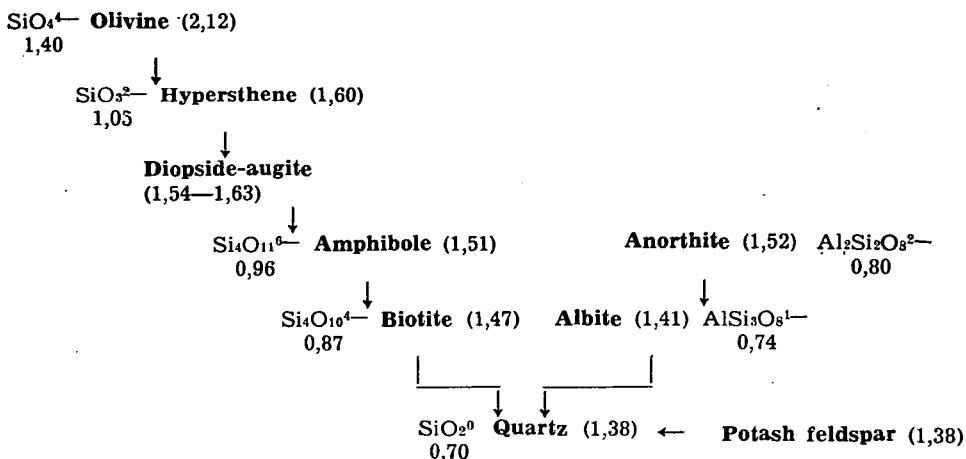


Fig. 1. The Bowen's reaction series of silicates with the corresponding compound potentials and ψ/SiO_4 potentials

potentials are to be taken into account, even the crystallization sequence: anorthite — albite — orthoclase can serve as example. This sequence corresponds to the sequence in order of the decreasing compound potentials. In the case of anorthite — albite, the succession may be explained merely by the difference between their ψ/SiO_4 values. Namely, the structure type of the two compounds is the same, the Al : Si ratio, however, in anorthite is 1 : 1 and in albite 1 : 3. Since the value of the ψ/SiO_4 potential increases by the increase of the rate of Al substitution, consequently the value characteristic of anorthite becomes higher than that of characteristic of albite.

However, in the case of albite — orthoclase both the structure type and the Al : Si ratio is the same in both compounds, therefore, the ψ/SiO_4 potential becomes in both compounds theoretically the same, consequently the crystallization sequence merely by this potential value can not be interpreted. In consequence, considering the silicates themselves, and not only the corresponding silicate anions, interpreting the crystallization sequence, the role of the cations can not be neglected. The common role and effect of the cations and the anions in a given compound can be taken into consideration and can be expressed by the compound potential introduced and applied to solution geochemical problems by Szádeczky-Kardoss (1954, 1955a, 1955b).

In accordance with the observations also on the basis of the compound potentials can be established that during the magmatic crystallization firstly the olivin crystallizes, belonging to the group of nesosilicates, followed by the separation of hypersthene belonging to the group of inosilicates (pyroxenes), then almost simultaneously begins the crystallization of the tectosilicates with the separation of Ca-plagioclase. Hence, firstly simple silicates without AlO_4 tetrahedra crystallize and the separation of silicates containing also AlO_4 tetrahedra begins later.

The process was explained by Szádeczky-Kardoss on the basis of the complex anionic potentials as follows. Of the Si^{4+} and Al^{3+} ions present in the magma owing to the higher ionic potential of the Si^{4+} ion related to that of the Al^{3+} ion, firstly the Si^{4+} ions form tetrahedral SiO_4^{4-} complexes. Therefore, firstly silicates not containing AlO_4^{5-} tetrahedra are formed like olivine and further pyroxenes. However, as soon as AlO_4^{5-} tetrahedra have been formed, beside the AlO_4^{5-} anion-free silicates also silicates rich in AlO_4^{5-} will be formed, since the AlO_4^{5-} anion has already higher anionic potential than the SiO_4^{4-} anion. Therefore, the basic plagioclases begin to separate, then follow the members of the plagioclase series and further the potassium feldspars. The AlO_4 content gradually decreases in this series, that is the Al : Si ratio in the anorthite is 1 : 1, whereas in the albite (and in orthoclase) 1 : 3, finally against an AlO_4^{5-} anion-free mineral, the quartz will be separated.

As it can be seen, on the basis of the compound potentials, two series is obtained; the one is the series of the colored rock-making minerals from olivine toward the biotite and the other is the series of the tectosilicates from the anorthite toward the quartz, and the separation of the silicates in these two series on the whole actually progresses according to the decreasing compound potentials as it has been stated by Szádeczky-Kardoss.

Examining the series obtained, arranging the corresponding silicate anions in order of the decreasing complex anionic potentials, the decrease of these values (Table 1) is continuous throughout the whole series from the nesosilicates toward the tectosilicates, that is the tectosilicates after the phyllosilicates are arranged into the series, whereas, arranging the minerals according to the decreasing compound potentials (Table 2), two series are obtained and the „potential level” of the anorthite approximately coincides with that of the inosilicates.

Should this fact mean that the statements to be drawn either on the basis of the complex anionic potentials or on that of the compound potentials regarding the crystallization sequence of silicate minerals of the Bowen series are contradictory to each other?

Or, should the approximate coincidence of the compound potential

Table 2.

The compound potentials of some silicate minerals according to Szádeczky-Kardoss

Silicate	Compound potential	Silicate	Compound potential
Discontinuous series:		Continuous series:	
<i>Nesosilicates-phyllsilicates</i>		<i>Tectosilicates</i>	
Olivine $(\text{Fe,Mg})_2\text{SiO}_4$	2,13	Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$	1,52
Hypersthene $\text{FeMgSi}_2\text{O}_6$	1,60	Albite $\text{NaAlSi}_3\text{O}_8$	1,41
Diopside $\text{CaMgSi}_2\text{O}_6$	1,54	Orthoclase KAlSi_3O_8	1,38
Amphibole $(\text{Mg,Fe,Ca})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	1,51	Quartz SiO_2	1,38
Biotite $\text{K}(\text{Mg,Fe,Al})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	1,47		

values of inosilicates and anorthite mean that the basic plagioclase can begin to separate always contemporaneously with the inosilicates, and should the compound potential value of KAlSi_3O_8 (1,38), which the lowest is in the series, mean that the separation of the potash feldspar can not start at an earlier stage of the crystallization? Or, the fact that among the colored constituents the biotite has the lowest compound potential (1,47) would mean that the biotite can be always crystallized as last member of the discontinuous series?

The sequence represented by the succession of minerals according to the decreasing compound potentials corresponds approximately to the normal case of differentiation of a gabbroic primary magma. In this series the biotite actually crystallizes as the latest member of the discontinuous series of colored constituents, and the separation of potash feldspar starts approximately at later stage of crystallization contemporaneously with that of albite and quartz, respectively.

However, taking into consideration the biotite diorite series, the most distinctive difference compared with the normal one mentioned above is partly the early appearance of biotite (before diopside, hypersthene and amphibole) and partly the lack of potash feldspar, whereas of the charnockite — anorthosite series the separation of potash feldspar even at early stage and the scarcity or missing of biotite and hornblende is characteristic.

A similar problem has arisen in *Keller's* paper (1954) regarding the relation between energy and mineral genesis. *Keller*, arranging the minerals of the *Bowen* series in order of increasing bonding energies adjusted to 24 oxygens, has stated that the position of some minerals (biotite and perhaps augite) is higher in the table showing the succession of the minerals than expected. *Keller* assumes that the sequence of crystallization of the minerals is „... the result of interplay, coordinated in time and space, of two factors, (1) the proper energy balance, and (2) the availability of an adequate concentration of appropriate elements.”

As it can be seen, though the succession of minerals of the *Bowen* series arranged in order of decreasing compound potentials shows not such discrepancy, nevertheless, it seems to be expedient, beside the compound potentials also other factors co-controlling the sequence of minerals to take into consideration.

In our opinion the succession of the different structure types, the succession of one-, two-, or three-dimensional Si—O—Al networks is marked only in principle by the ψ/SiO_4 potentials showing a continuously decreasing tendency throughout the series from the nesosilicates toward the tectosilicates and since the role of the cations is also to be taken into account, the succession of the silicate minerals themselves of the *Bowen* series likewise is marked merely theoretically by the decreasing compound potentials, however, what will be realized from these principal possibilities, depends, beside the compound potentials, upon other factors too.

In the following an attempt will be made to point to the possible connection between the variable ψ/SiO_4 potentials and the compound potentials, showing at the same time the factors too, which on interpreting the magmatic crystallization sequence of silicates beside the complex

anionic potentials and compound potentials, respectively, are also to be taken into account, as it has been mentioned also by *Keller* that such a manifold process as the magmatic crystallization can not be interpreted with merely one factor.

Several authors have dealt with the properties and nature of silicate melts. On the basis of the results of their investigations it is known that in the melt different structural elements are already present, i. e., it is presumable that before the beginning of the crystallization in the melt different silicate anions consisting of SiO_4 tetrahedra, linked together in different way, exist. It is also known that in a melt of pure silica the SiO_4 tetrahedra are linked in a three-dimensional framework and such a melt shows a relatively high viscosity. Adding Na_2O to this melt, however, the linking will decrease due to destroying the oxygen links and the three-dimensional framework breaks down into simpler groups under simultaneous decrease of the degree of viscosity. If by adding Na_2O to the melt, the Si : O ratio reaches 1 : 4, instead of the starting 1 : 2, the melt consists of independent SiO_4^{4-} tetrahedra and Na^+ ions and its viscosity becomes considerably lower than that of the original SiO_2 melt.

The degree of polymerization is markedly influenced by the $(\text{Si} + \text{Al}) : \text{O}$ ratio in the melt but an essential role may be attributed to the stability relations of the different silicate anions too, since the formation of an orthosilicate anion is associated with a lower energy release than the formation of a metasilicate anion and still greater energy is released when a phyllosilicate anion of type $\text{Si}_2\text{O}_5^{2-}$ is formed as it has been stated by *Ramberg* (1954).

As in the magma before the beginning of the crystallization silicate anion of different types are presumably present, the theoretical possibility of the simultaneous crystallization of silicates belonging to different structure types from the beginning is given. However, with progressive cooling of the magma, also the role and effect of the cations prevail.

At higher temperature, in earlier stage of crystallization firstly cations with higher ionic potential crystallize, linking chiefly to independent SiO_4 tetrahedra and inosilicate chains, respectively, as the Fe and Mg, but they can not be linked to three-dimensional Si—O—Al framework, to tectosilicate anions which preformed occasionally may also be present in the magma. On the other hand, cations with lower ionic potential as the Ca and especially the Na and K in general separate only later; the Ca is linked partly to silicate anions characteristic of inosilicates and partly, linked with the corresponding Si—O—Al framework, forms basic plagioclases, whereas the alkalies are linked mainly with silicate anions characteristic of tectosilicates and phyllosilicates, respectively.

Thus, in vain to assume the simultaneous presence of silicate anions of different types, among them the presence of three-dimensional Si—O—Al frameworks too, if such cations as the Fe and Mg capable to separate also in earlier period of the crystallization can not be linked to the three-dimensional framework, and on the other hand, to the separation of Ca, Na and K capable to link to such anions, the conditions are not favourable. Thus, in earlier stage of crystallization in general only simple

nesosilicates and inosilicates, respectively, separate and later under favourable conditions begins the crystallization of the alkalis, that is the crystallization of the tectosilicates containing also AlO_4 tetrahedra.

Ramberg has dealt with the problem why the Fe and Mg are connected rather with independent SiO_4 tetrahedra or with inosilicate chains but are not linked to three-dimensional framework, whereas the alkalis are mainly incorporated into tectosilicates and phyllosilicates, respectively. Here we wish only to refer to its corresponding work (Ramberg, 1952).

The general trend of crystallization mentioned above may be modified by different factors.

One of these factors is *the concentration of the cations* mentioned also by Keller (1954). The significance of the concentration of the cations is obvious also from the following example. The ψ/SiO_4 potential of the $\text{Si}_2\text{O}_7^{6-}$ anion characteristic of the sorosilicates is 1,22 or that of the $\text{Si}_6\text{O}_{18}^{12-}$ anion characteristic of the cyclosilicates (beryl) is 1,05, i. e., the theoretical possibility of the separation of the corresponding silicates, for example that of the thortveitite and beryl, respectively, at earlier stage of crystallization of the magma is given, however, owing to the low concentration of Sc and Be in the starting melt they remain in solution and are enriched in the residual liquid and the minerals mentioned will be occurred in the pegmatites when their concentration had reached an adequate level.

However, not alone the concentration but *the nature of the cations* is of importance too, since the bivalent cations and also the alkalis exert a significant influence by disrupting the Si—O bonds and breaking up the polymerized silicate anions into smaller units resulting the decrease of the viscosity as it is pointed out by Barth and Rosenquist (1949).

This effect of cations increases by increasing ionic potentials. The series according to decreasing ionic potential is as follows: Mg (2,56) — Fe (2,41) — Ca (1,89) — Na (1,02) — K (0,75).

Further, the viscosity of the magma is also to be taken into consideration. The viscosity is closely related to the degree of the linkage of SiO_4 tetrahedra. In general at given temperature the greater the degree of polymerization of SiO_4 tetrahedra and the greater the amount of more complex silicate anions in the magma, the higher its viscosity. At the same temperature an acid magma rich in three-dimensional silicate anions, rich in SiO_2 , has higher viscosity than a basic magma containing mainly simpler silicate complexes. The difference between the viscosity of acid and basic magmas exerts an essential influence on the process of the crystallization, since the velocity of diffusion and crystallization depends considerably upon the viscosity. In magmas with higher viscosity the migration of ions, the crystallization take place presumably rather retarded than in magmas with lower viscosity. Therefore, it may be imagined that this fact too has an influence, inasmuch as in acid magmas, rich in three-dimensional Si—O—Al frameworks, the plagioclase feldspars and in general the tectosilicates, during the magmatic crystallization only later, approximately contemporaneously with the inosilicates begin to crystallize. On the contrary, the lower viscosity of basic magmas

containing rather simpler silicate complexes favours and promotes the process of crystallization, and so perhaps the earlier crystallization of the tectosilicates could be interpreted.

SUMMARY

Interpreting the magmatic crystallization sequence on the basis of the compound potentials introduced by *Szádeczky-Kardoss* it may be assumed that the possible sequence of different silicates is given only in principle by the complex anionic and the compound potentials, respectively. However, it seems to be expedient beside these factors also others co-controlling the crystallization sequence of the silicates to be taken into account. Presumably the following factors are to be taken into consideration:

a) the variable ψ/SiO_4 potentials by which partly the stability relations of the different silicate anions present in the magma and partly the succession of formation of these anions may be marked,

b) the compound potentials by which the resultant effect of the cation and the anion in a given compound can be characterized and by which it is indicated when a given silicate in the reaction series can be separated.

c) The sequence of minerals in order of the decreasing compound potentials is only the theoretically probable succession of the minerals which succession is modified on interaction of other factors such as the concentration and nature of the cations present in the magma, since, in vain the different silicate anions are present in the magma at the beginning of the crystallization, if the concentration of appropriate elements do not reach an adequate level. In such cases, though the separation of a given compound according to its compound potential value, would be possible at a relatively earlier stage of the crystallization, it will be separated only at later stage if the cation, enriched in residual liquid, reaches an adequate concentration. The nature of the cations is also essential, since the cations (bivalent cations and alkalies and also the volatiles) breaking down the polymerized silicate anions into smaller units diminish the degree of viscosity of the magma.

d) As it was seen, a close interaction exists among the concentration and nature of the cations, the basic or acid character of the magmas, the degree of polymerization of SiO_4 tetrahedra. The resultant effect of the interaction of these factors is revealed in the change of the degree of the viscosity of the magmas which may exert an essential effect on the process of differentiation influencing the velocity of the migration of ions and the crystallization.

In the further examinations an effort will be made to attempt to explain the connection between the sequence of crystallization of silicates and the controlling factors — the interaction of factors mentioned was explained only qualitatively in this paper — at least in a semi-quantitative manner.

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