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

Part I. The variability of the complex anionic potentials*

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1. INTRODUCTION

The Cartledge's ionic potential is the quotient of the charge and the radius of the cation, that is

$$\psi = \frac{z}{r}.$$

Szádeczky-Kardoss (1954) has pointed out that analogously may be calculated also the ionic potential of the simple and complex anions, respectively, and the values obtained would be just as charactereistic of the anions as the cationic potentials characterize the cations. Correspondingly, the complex anionic potential is the quotient of the charge and radius of the complex anion.

Szádeczky-Kardoss (1954), introducing the concept of the complex anionic potential, has used the Fersman's complex anionic radii used also by *Saukow* (1953). These radii, however, are rather computed on the basis of additivity of the Goldschmidt's ionic radii and not determined on the basis of the measured actual ionic distances within the complex anion.

Taking into consideration the complex anions as the building elements of crystal lattices it is well known that the bonding within the complex anions, that is, between the central cation and oxygen, is not dominantly ionic but to some extent covalent. Therefore, the distance central cation-oxygen can not be given additively from the radii of the cation and oxygen, thus nor can the complex anionic potential be computed on the basis of simple additivity of radii.

In the sets of BO_3^{3-} — CO_3^{2-} — NO_3^{1-} ions or SiO_4^{4-} — PO_4^{3-} —

$SO_4^{2-} - ClO_4^{1-}$ ions the ionic character of the A—O bonds becomes gradually less and correspondingly more considerable the covalent character with increasing charge and decreasing radius of the central cation that is with its increasing cationic potential and with decreasing difference between the electronegativity values of the central cation and the oxygen anion. Due to the increasing polarizing effect of the central cation the deformation of the oxygen ion becomes stronger.

These changes, however, naturally can not be expressed by the complex anionic potential calculated on the basis of simple additivity of the ionic radii.

2. THE CHANGE OF THE IONIC DISTANCES WITHIN THE COMPLEX ANIONS. THE COMPUTATION OF THE COMPLEX ANIONIC POTENTIAL

Considering the polarization of the complex anions in crystals beside the polarizing power of the central cation must be taken into consideration also the contrapolarizing effect of the neighbouring cations connected to the oxygen of the complex anion. The contrapolarization may result the increase of the ionic distance within the complex, moreover in some cases may hinder the formation of complex anions. Thus the P—O distance in PO_4^{3-} in average is 1,56 Å. In the PO_4^{3-} anion according to Pauling the resonance of single and double covalent as well as ionic bonds can be supposed. In the lattice of Ag_3PO_4 the covalent character of the Ag—O bonds due to the contrapolarizing effect of Ag, however, hinders the formation of the P—O double covalent bonds within the complex and consequently the P—O distance in the Ag_3PO_4 increases to 1,61 Å and in the lattice of YPO_4 becomes 1,71 Å owing to the increased polarizing power of the neighbouring cation. This latter distance is almost equal to the sum of ionic radii (1,73 Å). It has been mentioned that neighbouring cations of strong contrapolarizing power may hinder the formation of complex anions. Thus, e. g., in the lattice of Li_2MoO_4 the real MoO_4^{2-} complex anion exists, whereas in the lattice of Ag_2MoO_4 the strong contrapolarizing effect of Ag makes impossible the formation of the MoO_4^{2-} complex anion and this compound means transition to the simple coordination structure of spinel-type (*Hiller*, 1952).

The character of the bonding and the variation of the ionic distances within the complexes in crystals depends on the contrapolarizing effect and coordination number of the neighbouring cations as well as on the polarizing power of the central cation and on other factors.

As the same complex anion in its different compounds may be connected with various cations of different coordination number and contrapolarizing power, the ionic distances in complex anion — also in the case of the same complex — may change from compound to compound and hence may also change the value of the complex anionic potential.

Thus the radius of the complex anion must be calculated on the basis of ionic distances measured roentgenographically and therewith the effect

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of the factors above-mentioned to the change of ionic distances implied is also taken into consideration.

The necessity of the refinement of this kind of the computations has been shown also by *Szádeczky-Kardoss* (1954): „Bei der Berechnung von Tabelle III wurden übrigens die allgemeine gebräuchliche Ionenradien angewandt. Diese Zahlen können und müssen aber später verfeinert werden, u. zw. mit den von dem kovalenten bzw. heteropolaren Verbindungstyp, ferner mit den von der Koordinationszahl usw. abhängenden tatsächlichen Ionenabmessungen . . .".

Similarly refer *Leutwein* and *Doerffel* (1956) that Fersman's computation-method regarding to the radii of complex anions as well as to the complex anionic radii used by *Saukow* (1953) cannot give accurate results since the change of ionic distances within the complexes due to the factors above-mentioned is not taken into consideration by this method and is not expressed by the values obtained.

The authors mentioned above and also others state that accurate radius values may only be obtained on determining the ionic distances from X-ray measurements or from molrefractions and computing the radius of the complex anions on the basis of these data. In this case the radius,

$$r = 2a - r_c,$$

where r is the radius of the complex anion, a the ionic distance measured and r_c the radius of the central cation.

Bearing in mind the actual ionic distances, the potential of complex anions in crystals may be calculated from the following equation:

$$\psi_{complex} = \frac{z_c - n \cdot z_a}{2a - r_c},$$

where z_c and z_a mean the charges of the cation and anion, respectively n is the number of anions in the complex around the central cation of radius r_c.

The central cation in general is of small size and highly charged, that is, less polarizable, its radius can be considered as constant in various compounds of the same complex anion. The values given for the cationic radii in the different tables generally regard to 6-coordinated cations. Therefore if tetrahedral oxyanions are in question at the calculation of the potential and radius of the complex anions, the radius of the central cation must be corrected to 4-coordination. Calculating, however, the complex anionic potential of the single tetrahedral oxyanions and using for the central cation the radius values valid for 6-coordination number, the error will not be essential. Thus, e. g., in the following set, the number after the complex anion means the anionic potential computed with the radius value corrected for 4-coordination number and the value in parenthesis means the potential calculated with the radius valid for 6-coordination:

MgO_4^{6-} 1,75 (1,73); TiO_4^{4-} 1,16 (1,14); AlO_4^{5-} 1,52 (1,51); SiO_4^{4-} 1,25 (1,24); PO_4^{3-} 0,95 (0,95); CrO_4^{2-} 0,60 (0,60).

Intending, however, to calculate the compound potentials according to *Szádeczky-Kardoss* (1954), beside the potential of the complex anions also the potential of the neighbouring cations must be taken into calculation, the coordination number of the cations can not be neglected any more as it could yield essential differences in the numerical value of the compound-potential. This is one of the ways of the further refinement of the calculation-method of the compound potentials. It is well known that the change of the coordination number results in the change of the cationic radius and consequently will change also the cationic potential. For example, the cationic potential of the 4-coordinate Ca^{2+} ion is 2,15, that of the 6-coordinated 2,02 and that of the 9-coordinated is 1,90.

The complex anionic potentials calculated on the basis of the actual ionic distances found in the various crystals are rather characteristic of the complex anions than the potential values deduced on the basis of the additivity of the ionic radii. But this calculation too, is to some extent of approximative character since at the calculations the complex anions are considered as rigid spheres and the possible deformation of the tetrahedral oxyanions — resulting the variation of the central cation-oxygen distances in all the four directions — at the most in that manner is taken into account that it is calculated with the mean value of the central cation-oxygen distances of four kinds.

Thus, the polarization revealed in the shortening of the ionic distances not only must but also can be taken into consideration calculating the potential of complex anions existing in different compounds as elements of the lattice in all cases, when the ionic distances are given from X-ray measurements.

In geochemical relations, however, not alone the comparison of the complex anions as elements of crystals is needed on the basis of their complex anionic potential but efforts are made to study the behaviour of the complexes also in the magma, wherein complex anions preformed already exist.

It can be assumed, that the polarization in the case of these independent oxyanions in melts is stronger than in solid crystals due to the onesided polarizing effect of the central cation.

Now the question arises, what degree of polarization must be supposed and with what ionic distances must be calculated the radius of the complex anions and further their potential values?

It would be possible to calculate the radius and the potential on the basis of ionic distances valid in the lattices of the different compounds of the given complex anion. These distances, however, according to the data given in Tables 1—7 change from compound to compound, thus, e. g., the P—O distance in PO_4^{2-} anion varies between 1,44—1,71 Å the S—O distance in SO_4^{2-} anion between 1,44—1,60 Å, the Si—O distance in the SiO_4^{4-} anion changes beween 1,54—1,77 Å in their different compounds.

Calculation with the average of these ionic distances in the case of independent oxyanions existing in melts would mean the account the polarization to some extent. But to apply the ionic distances measured in solid crystals to independent complex anions in melts would mean

also some arbitrariness since the formation and the change of ionic distances within the complex anions in lattices is resulted not alone by the polarizing power of the central cation but also by the contrapolarizing effect of the neighbouring cations and this latter effect depends upon the size, charge and coordination number of the cation. In the melts, however, the complex anions exist as independent units and are not yet joined with cations.

Thus would complex anions in melts as independent units be in question the complex anionic potential may be calculated on the basis of ionic model although the polarization, the covalent character of the bonds is not expressed by the potential values computed in this manner. It is obvious that these complex anionic potentials in their numerical values do not correspond the values that would be obtained having data relating to ionic distances measured within the different complex anions in melts. Failing these data, however, instead of doubtful assumptions the ionic model can serve at least as uniform basis of comparison.

The complex anionic potential on the basis of ionic model:

$$\psi_{complex} = \frac{z_c - n \cdot z_a}{2r_a + r_c},$$

where r_a and r_c mean radii of the anion and the cation, respectively, z_a and z_c mean their charges and n is the number of anions around the central cation.

Though the application of ionic model at the calculation of complex anionic potential in the case of independent complex anions in melts

Table 1.

The variability of the radius and anionic potential of some complex anions.

Complex anion	Values[1] according to Szádeczky—Kardoss		Values[2] calculated on the basis of additivity of ionic radii		New values[2] calculated taking into account the actual ionic distances						Number of the compounds examined
					r			ψ			
	r	ψ	r	ψ	min.	max.	av.	min.	max.	av.	
AlO_4^{5-}	3,15	1,59	3,28	1,52	2,82	3,08	2,92	1,62	1,77	1,71	10
SiO_4^{4-}	2,90	1,38	3,20	1,25	2,82[3]	3,15[3]	2,94[3]	1,24[3]	1,41[3]	1,35[3]	13[3]
BO_3^{3-}	2,68	1,12	3,01	0,99	2,29	2,67	2,50	1,12	1,31	1,19	11
AsO_4^{3-}	2,95	1,02	3,23	0,92	2,83	3,07	2,93	0,97	1,06	1,02	13
PO_4^{3-}	3,00	1,00	3,13	0,95	2,55	3,09	2,79	0,97	1,17	1,07	15
CO_3^{2-}	2,57	0,77	2,95	0,67	2,31	2,19	2,40	0,80	0,86	0,82	8
SO_4^{2-}	2,95	0,68	3,08	0,64	2,60	2,92	2,76	0,68	0,77	0,72	16
CrO_4^{2-}	3,00	0,67	3,29	0,60	2,71	2,85	2,74	0,70	0,73	0,72	6
NO_3^{1-}	2,57	0,39	2,92	0,34	2,30	2,38	2,34	0,42	0,43	0,42	4

[1] On the basis of Goldschmidt's cationic radii and Fersman's anionic radii
[2] On the basis of Ahrens's cationic radii and Pauling's oxygen ionic radius
[3] The values are related to the nesosilicates

is obviously but necessary solution, some problems may be approximately explained and interpreted also on this basis as the stability relations of the tetrahedral complex anions, the periodicity of the anionic potentials, the connection between the electrostatic energy and the anionic potential of the tetrahedral complex oxyanions.

The differences among values calculated on the basis of ionic model and of the average of actual ionic distances measured in lattices of different compounds of anisodesmic (and mesodesmic) structures are given in Table 1.

In the Table 1 are also denoted the minimal, maximal radius and potential values of the complex anions calculated on the basis of ionic distances measured in different lattices.

3. THE VARIATION OF SOME COMPLEX ANIONIC POTENTIALS IN ANISODESMIC STRUCTURES

The complex anionic potential values of some complex anions characteristic of anisodesmic structures are summarized in Tables 2—7 on the basis of X-ray measurements found in the literature. As in many cases the tetrahedron is distorted, computing the anionic radii and the anionic potentials the mean value of the ionic distances determined, was taken into consideration. In the Tables are denoted also the ionic distances, the anionic radii and potential values, respectively, calculated from simple ionic model.

For the cationic radii the Ahrens's values corrected to 4-coordination and for the radius of oxygen anion the Pauling's value of 1,40 Å were used.

Table 2.

The complex anionic potential of the CO_3^{2-} ion in some compounds

Ionic distance:	1,55 Å
Radius:	2,95 Å
Anionic potential:	0,67

(All the three values are calculated from ionic model.)

Compound	C—O distance	r_{CO_3}	ψ_{CO_3}	References
PbCO₃ Cerussite	1,23	2,31	0,86	Landolt · Börnstein (1955)
(Ce,La...)FCO₃ Bastnäsite	1,25	2,35	0,84	Oftedal (1930)
Na₂CO₃ . NaHCO₃ . 2H₂O	1,25	2,35	0,84	Structure Rep. vol. 12.
PbCl₂CO₃ Phosgenite	1,25	2,35	0,84	Structure Rep. vol. 10.
CaCO₃ Calcite	1,29	2,43	0.82	Landolt—Börnstein (1955)
CaCO₃ Aragonite	1,30	2,45	0,81	Landolt - Börnstein (1955)
Ca₂Na₂(CO₃)₃ Shortite	1,31	2,47	0,80	Structure Rep. vol. 12.
KAgCO₃	1,32	2,49	0,80	Structure Rep. vol. 9.
Average	1,28	2,40	0,82	

Table 3.

The complex anionic potential of the NO_3^{1-} ion in some compounds

Ionic distance :	*1,55* Å
Radius :	*2,95* Å
Anionic potential	*0,67*

(All the three values are calculated from ionic model.)

Compound	N—O distance	r_{NO_3}	ψ_{NO_3}	References
TlNO₃	1,21	2,30	0,43	Structure Rep. vol. 9.
Pb(NO₃)₂	1,22	2,32	0,43	Landolt—Börnstein (1955)
NaNO₃	1,25	2,38	0,42	Leutwein and Doerffel (1956)
LiNO₃	1,25	2,38	0,42	Pauling and Huggins (1934)
Average	1,24	2,34	0,42	

Table 4.

The complex anionic potential of the PO_4^{3-} ion in some compounds

Ionic distance :	*1,73* Å
Radius :	*3,13* Å
Anionic potential :	*0,95*

(All the three values are calculated from ionic model.)

Compound	P—O distance	r_{PO_4}	ψ_{PO_4}	References
BPO₄	1,44	2,55	1,17	Heritsch (1940)
Al(PO₃)₃	1,51	2,69	1,11	Pauling and Sherman (1937)
(Ce,La,Pr)PO₄ Monazite	1,52	2,71	1,10	Structure Rep. vol. 9.
Li(Fe₁₋ₓ,Mnₓ)PO₄ Triphylite	1,53	2,73	1,09	Structure Rep. vol. 13.
AlPO₄	1,54	2,75	1,09	Wyckoff (1951)
Zr₂P₂O₇	1,54	2,75	1,09	Heritsch (1940)
Ba₃(PO₄)₂	1,56	2,79	1,07	Wyckoff (1951)
Sr₃(PO₄)₂	1,56	2,79	1,07	Wyckoff (1951)
KH₂PO₄	1,56	2,79	1,07	Landolt—Börnstein (1955)
NH₄H₂PO₄	1,58	2,83	1,06	Wyckoff (1951)
Ag₃PO₄	1,61	2,89	1,03	Structure Rep. vol. 9., 11.
Cu₂(OH)PO₄ Libethenite	1,61	2,89	1,03	Heritsch(1940)Wyckoff(1951)
Fe₃(PO₄)₂ . 8H₂O Vivianite	1,62	2,91	1,03	Structure Rep. vol. 13.
NaMnPO₄ Natrophilite	1,62	2,91	1,03	Structure Rep. vol. 9.
YPO₄ Xenotime	1,71	3,09	0,97	Hiller (1952)
Average	1,56	2,79	1,07	

Table 5.

The complex anionic potential of the SO_4^{2-} ion in some compounds

Ionic distance:	*1,68* Å
Radius:	*3,08* Å
Anionic potential:	*0,64*

(All three values are calculated from ionic model.)

Compound	S—O distance	r_{SO_4}	ψ_{SO_4}	References
$K_2Pb(SO_4)_2$ Palmierite	1,44	2,60	0,77	Structure Rep. vol. 11., 13.
$Th(OH)_2SO_4$	1,47	2,66	0,75	Structure Rep. vol. 13.
Ag_2SO_4	1,48	2,68	0 74	Zachariasen (1932)
Na_2SO_4	1,49	2,70	0.74	Structure Rep. vol. 9.
$CaSO_4.2\ H_2O$ Gypsum	1,49	2,70	0,74	Wooster (1936)
K_2SO_4	1,50	2,72	0,73	Landolt Börnstein (1955)
$Li_2SO_4.H_2O$	1,50	2,72	0,75	Ziegler (1934)
$BeSO_4.H_2O$	1,50	2,72	0,75	Beevers, Lipton (1932)
$KAl(SO_4)_2.12\ H_2O$	1,52	2,75	0,72	Landolt—Börnstein (1955)
$NiSO_4.7\ H_2O$	1,52	2,76	0,72	Beevers, Schwartz (1935)
$SrAl_3(SO_4)(PO_4(OH)_6$ Svanbergite	1,54	2,80	0,71	Structure Rep. vol. 11.
$CaAl_3(PO_4)(SO_4)(OH)_6$ Woodhouseite	1,54	2,80	0,71	Structure Rep. vol. 11.
$NaKSO_4$ Aphthitalite	1,60	2,92	0,68	Structure Rep. vol. 9.
$(NH_4)_2Mg(SO_4)_2.6\ H_2O$	1,60	2,92	0,68	Landolt Börnstein (1955)
$Na_8Al_6Si_6O_{24}.SO_4$ Nosean	1,60	2,92	0,68	Barth (1933)
$CaSO_4$ Anhydrite	1,60	2.92	0 68	Wyckoff (1951)
Average	1,52	2,76	0,72	

Table 6.

The complex anionic potential of the CrO_4^{2-} ion in some compounds

Ionic distance:	*1,89* Å
Radius:	*3,29* Å
Anionic potential:	*0,60*

(All the three values are calculated from ionic model.)

Compound	Cr—O distance	r_{CrO_4}	ψ_{CrO_4}	References
Na_2CrO_4	1,60	2,71	0,73	Miller (1936)
K_2CrO_4	1,60	2,71	0,73	Zachariasen and Ziegler(1931)
Rb_2CrO_4	1,60	2,71	0,73	Smith and Colby (1941)
Cs_2CrO_4	1,60	2,71	0,73	Miller (1938)
$CaCrO_4$	1,64	2,79	0,71	Clouse (1933)
$CuCrO_4$	1,67	2,85	0,70	Structure Rep. vol. 9.
Average	1,61	2,74	0,72	

Table 7.

The complex anionic potential of the AsO$_4^{3-}$ ion in some compounds

Ionic distance:	1,83 Å	
Radius:	3,23 Å	
Anionic potential:	0,92	

(All the three values are calculated from ionic model)

Compound	As—O distance	r_{AsO_4}	ψ_{AsO_4}	References
BiAsO$_4$	1,63	2,83	1,06	Structure Rep. vol. 11.
Cu$_2$(OH)AsO$_4$ Olivenite	1,63	2,83	1,06	Heritsch (1938)
Fe$_3$(AsO$_4$)$_2$. 8 H$_2$O Symplesite	1,64	2,85	1,05	Structure Rep. vol. 13.
BAsO$_4$	1,66	2,89	1,03	Wyckoff (1951)
AlAsO$_4$	1,66	2,89	1 03	Wyckoff (1951)
Ca$_2$Na(Mg,Mn)$_2$(AsO$_4$)$_3$ Berzeliite	1,68	2,93	1,02	Bubeck. Machatschki (1935)
NaAlFAsO$_4$ Durangite	1,68	2,93	1,02	Kokkoros (1938)
FeAsO$_4$. 2 H$_2$O Scorodite	1,69	2,95	1,01	Structure Rep. vol. 11.
Zn(ZnOH)AsO$_4$ Adamite	1,70	2,97	1,01	Heritsch (1938)
Fe$_4$(OH)$_2$(AsO$_4$)$_3$K . 6—7 H$_2$O Pharmacosiderite	1,71	2,99	1,00	Structure Rep. vol. 11.
YAsO$_4$	1,73	3,03	0,99	Heritsch (1938)
KH$_2$AsO$_4$	1,74	3,05	0,98	Wyckoff (1951)
Ag$_3$AsO$_4$	1,75	3,07	0,97	Structure Rep. vol. 9., 11.
Average	1,68	2,93	1,02	

As it may be seen from Table 1 there is sometimes a significant difference among the minimal, maximal and average values of the radii and potentials of the complex anions computed from measured ionic distances and the corresponding values calculated on the basis of ionic model. Thus, e. g., the average value of the radius of PO$_4^{3-}$ anion is 10,8 per cent lower than that of computed from ionic model. Correspondingly the average complex anionic potential is 11,2 per cent higher than that of calculated on the basis of ionic model. Even the minimal and maximal potential values reckoned from actual ionic distances show a fluctuation of about ± 9 per cent relating to the average value.

These data included in the Tables seem to be enough to verify that the radius and consequently the potential of the same complex anion can change from compound to compound. Thus, computing the complex anionic potentials — especially intending to calculate the compound-potential of the given compound too — seems to be expedient to reckon on the basis of the actual ionic distances determined in the complex anion. It is obvious that the *Szádeczky-Kardoss's* compound-potential values — which are essentially composed of the potential values of the ingredient elements of the compounds and can be considered as the

arithmetical mean of these potential values — will be the more characteristic of each compound the more the relations valid in the lattice of the compound in question are taken into account.

4. THE VARIABILITY OF THE ANIONIC POTENTIAL OF SiO_4^{4-} ANION IN MESODESMIC SILICATES

A. The change of the properties of the tetrahedral SiO_4^{4-} anion in the various types of silicates due to their polymerization

Silicates are characterized partly by the presence of SiO_4 tetrahedra partly by the degree of polymerization. From the nesosilicates toward the tectosilicates by increasing polymerization increases the number of shared oxygens per silicon tetrahedron. While the nesosilicates are characterized by discrete SiO_4 tetrahedra not linked directly together, in the lattice of tectosilicates the polymerization reaches the highest degree.

The SiO_4 anion possesses presumably other properties in such a lattice wherein only discrete SiO_4 groups exist connected only with cations like in the nesosilicates and in those structures wherein all of the oxygens are common with two tetrahedra like in the tectosilicates to mention merely the two extreme types.

Should the anionic potentials correctly characterized the properties of complex anions — as shown by *Szádeczky-Kardoss's* so far results (1954, 1955a, 1955b, 1958) — the change of the properties of the SiO_4 tetrahedra, effected by the gradual polymerization, had to be expressed by the change of the numerical value of the complex anionic potential.

Schaefer, Matossi and *Wirtz* (1934) as well as *Matossi* and *Krüger* (1936) studying the infrared reflection spectra of silicates of different structural types stated as follows: „Zwischen 8 und 12 μ tritt bei allen Silikaten eine Reflexionsbande auf, die wir der dreifachen kurzwelligen aktiven Eigenschwingung des SiO_4-Tetraeders zuschreiben; die Aufspaltung dieser Bande wechselt sehr von Silikat zu Silikat. Im Einklang mit der Feststellung in I erkennt man, dass mit steigender Verknüpfung der SiO_4-Tetraeder eine Tendenz zur Verschiebung nach kürzeren Wellen besteht, die zwar manchmal, besonders bei Übergangsstrukturen verwischt wird, bei einer Auswahl typischer Vertreter der einzelnen Strukturen aber deutlich zum Ausdruck kommt."

Fig. 1 showing the shift of the reflection bands characteristic of SiO_4 tetrahedron toward the shorter wawe lengths by increasing grade of polymerization from the nesosilicates to the tectosilicates is drawn on the basis of the data of the papers mentioned above. In Fig. 1 the thicker lines mean the relatively strong maxima and the thin lines the less strong ones.

Keller, Spotts and *Biggs* (1952) dealt with the infrared absorption spectra of some common carbonates, sulphates, phosphates and silicates. On the influences of the cation and the anion on the spectra they state as follows: „Just as the crystal architecture is dominated by the larger

oxygen-containing anions, so are the absorption spectra dominated by the bonds between the oxygen and the element which characterizes the anion. The cations exert only a secondary influence. From another viewpoint, the infrared absorption spectra owe their origin to the covalent bonding which is accentuated in the anions." Of their discussion of silicate spectra from our point of view the following statements are of importance: ,,The position of the strongest absorption band by the silicate radical shifts slightly but regularly toward longer wave lengths from tectosilicates to nesosilicates, the cyclosilicates excepted because they vary within themselves. As the number of shared oxygens per silicon tetrahedron decreases, and as the number of aluminum and other non-silicon atoms injected into the silica assemblage increases, the position of the strong absorption bands shifts toward longer wave lengths."
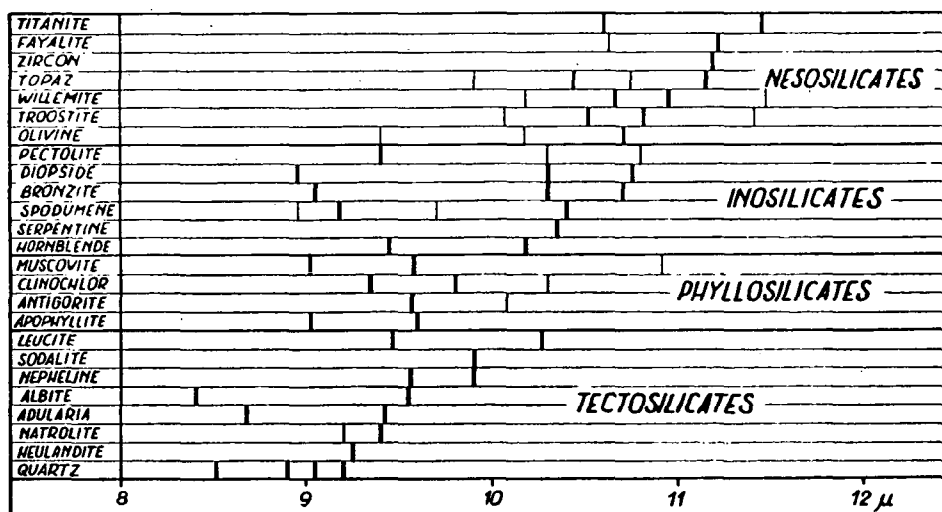
Fig. 1. The shift of the reflection bands in the infrared reflection spectra of the silicates depending upon the degree of silification.

The change of the properties of the SiO_4 group influenced by the type of linkage is also pointed out by *Huggins* and *Sun* (1946) establishing the change of energy constant of Si^{4+} ion depending on the structure type. Thus the values of the r_{Si} in the different structures are the following: nesosilicates — 3142 kg. cal.; sorosilicates — 3137 kg. cal.; inosilicates — 3131 kg. cal.; phyllosilicates — 3123 kg. cal.; tectosilicates (SiO_2) — 3110 kg. cal.

Ramberg (1952, 1954) has pointed out that the degree of polarization of oxygen ions varies depending on the polymerization. The more polarized is the oxygen the more stable are the silicates.

The change of the properties of the SiO_4 group owing to the linkage of the SiO_4 tetrahedra is both theoretically and experimentally proved.

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The anionic potential of SiO_4^{4-} anion till now both in nesosilicates and in tectosilicates amounted to 1,38. Therefore, it seems to be obvious that this constant value can not characterize the SiO_4^{4-} anion existing in the different silicates of different structure types. Hence, it had to be found the possibility to express the variable properties of SiO_4 anion by the complex anionic potential.

The study of the variability of the anionic potential of SiO_4^{4-} anion in the different silicates is more essential than that of in the case of complex anions characteristic of anisodesmic structures, owing to the geochemical and petrographical importance of silicates.

It has been shown that the complex anionic potentials are variable and that this variability is the result of the change of the character of the bonding in the anion. This change is expressed by the shortening or lengthening of the ionic distances in the anion.

In the value of the anionic potential of SiO_4^{4-} in the silicates of different structure types may also be stated a fluctuation caused by the same factor. As it can be seen in Table 8 the Si—O distance varies between 1,61—1,81 Å in the nesosilicates, correspondingly does the anionic potential between 1,42—1,24 too. The value computed on the basis of Fersman's anionic radius is 1,38.

In our opinion, however, in the case of silicates as well as borates, beside the change of this kind of the anionic potential, is rather important an other change depending firstly on the structural pecularities of the silicates and borates. This change of the complex anionic potential both in its numerical value and in geochemical significance means a much greater change than the one depending mainly upon the change of the ionic distances.

Let us focus our consideration partly the SiO_4 tetrahedron present with variable properties in all structure types of silicates, partly the change of its properties depending on the degree of linkage of the tetrahedra, that is on the degree of silification.

Therefore, computing the anionic potential values characteristic of the SiO_4 tetrahedra in the different structure types, the degree of the silification had to be taken into consideration by regarding the number of the shared oxygens per silicon tetrahedron.

The potential values new computed are designated as ψ/SiO_4 potentials to express in this way too that the values refer always to the single SiO_4 groups existing in the various structures.

B. The calculation of the ψ/SiO_4 potentials

The average Si—O distance taking into consideration the silicates of different types according to the data of Table 8 is 1,62 Å. The complex anionic radius computed from this distance is 2,84 Å and the anionic potential is 1,40. Attempting only to illustrate the principle of the method applied for calculations in further discussions, in the case of all structural types this mean value will be used as starting value. In the case of calculations relating to given silicates naturally the calculations must be made on the basis of ionic distances valid in the given silicates including

in this manner also the change of the potential value caused by the change of the ionic distances. Thus by computing the ψ/SiO_4 potentials in Table 8 the effects on the change of complex anionic potential caused by both the ionic distances and the grade of polymerization in the given silicates were taken into calculation.

a) Nesosilicates

As in the lattice of nesosilicates independent separate SiO_4 tetrahedra exist, not linked directly together only by cations, the complex anionic potential is 1,40. As it has been mentioned, in the nesosilicates the change of the anionic potential depends mainly on the change of the ionic distances (Fig. 2.)

[SiO₄]⁴⁻

Fig. 2.

[Si₂O₇]⁶⁻
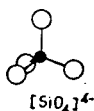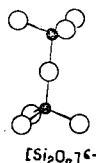
Fig. 3.

Table 8.

The change of the Si—O distance as well as that of the radius and anionic potential of the SiO_4^{4-} anion in some silicates.

Silicate	Si—O distance	r_{SiO_4}	ψ_{SiO_4}	ψ/SiO_4	References
Nesosilicates		Complex anion: SiO_4^{4-}			
Andalusite Al_2OSiO_4	1,61	2,82	1,41	1,41	Landolt—Börnstein (1955)
Disthene Al_2OSiO_4	1,62	2,84	1,40	1,40	Landolt—Börnstein (1955)
Titanite $CaTiOSiO_4$	1,62	2,84	1,40	1,40	Landolt—Börnstein (1955) Wyckoff 1951)
Zircon $ZrSiO_4$	1,62	2,84	1,40	1,40	Landolt—Börnstein (1955)
Willemite Zn_2SiO_4	1,62	2,84	1,40	1,40	Bragg and Zachariasen (1930)
Phenacite Be_2SiO_4	1,62	2,84	1,40	1,40	Bragg and Zachariasen (1930)
Uvarovite $Ca_3Cr_2(SiO_4)_3$	1,66	2,93	1,36	1,36	Menzer (1929)
Andradite $Ca_3Fe_2(SiO_4)_3$	1,67	2,95	1,35	1,35	Menzer (1929)
Eucryptite $LiAlSiO_4$	1,69	2,98	1,34	1,34	Structure Rep. vol. 11.
Pyrope $Mg_3Al_2(SiO_4)_3$	1,72	3,05	1,31	1,31	Menzer (1929)
Almandite $Fe_3Al_2(SiO_4)_3$	1,72	3,05	1,31	1,31	Menzer (1929)
Spessartite $Mn_3Al_2(SiO_4)_3$	1,74	3,09	1,29	1,29	Menzer (1929)
Grossularite $Ca_3Al_2(SiO_4)_3$	1,77	3,15	1,27	1,27	Menzer (1929)
Olivine $(Mg,Fe,Mn)_2SiO_4$	1,81	3,22	1,24	1,24	Landolt—Börnstein (1 955)

Silicate	Si—O distance	r_{SiO_4}	ψ_{SiO_4}	ψ/SiO_4	References
Sorosilicates		Complex anion: $Si_2O_7^{6-}$			
Thortveitite $Sc_2Si_2O_7$	1,60	2,80	2,50	1,25	Landolt—Börnstein (1955)
Hemimorphite $Zn_4(OH)_2Si_2O_7 \cdot H_2O$	1,63	2,86	2.44	1,22	Ito (1933)
Lawsonite $CaAl_2(OH)_2Si_2O_7 \cdot H_2O$	1,65	2,90	2.41	1,20	Structure Rep. vol. 11.
Lievrite $CaFe_2^{II}Fe^{III}(OH)OSi_2O_7$	1,74	3,09	2.26	1,13	Structure Rep. vol. 11.
Cyclosilicates		Complex anions: $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$			
Beryl $Be_3Al_2Si_6O_{18}$	1,58	2,76	6,51	1,08	Bragg (1930) Structure Rep. vol. 13.
Benitoite $BaTiSi_3O_9$	1,62	2,84	3,16	1.05	Zachariasen (1930)
Inosilicates		Complex anions: $Si_2O_6^{4-}$ and $Si_4O_{11}^{6-}$			
Enstatite $Mg_2Si_2O_6$	1,58	2,76	2,16	1,08	Warren and Modell (1930)
Spodumene $LiAlSi_2O_6$	1,60	2,80	2,15	1,07	Structure Rep. vol. 9. and 13.
Ramsayite $Na_2Ti_2O_3Si_2O_6$	1,62	2,84	2,12	1,06	Warren and Biscoe (1931)
Hypersthene $(Fe,Mg)_2Si_2O_6$	1,62	2,84	2,12	1,06	Landolt—Börnstein (1955)
Diopside $CaMgSi_2O_6$	1,65	2,90	2,07	1,03	Warren and Bragg (1929), Bragg (1930), Landolt—Börnstein (1955)
Anthophyllite $(Mg,Fe)_7(Si_4O_{11})_2(OH)_2$	1,62	2,84	3,87	0,96	Structure Rep. vol. 13.
Phyllosilicates		Complex anion: $Si_4O_{10}^{4-}$			
Muscovite* $KAl_2(OH,F)_2(AlSi_3O_{10})$	1.60	2,80	3,70	0,92	Landolt—Börnstein (1955)
Pyrophyllite $Al_2(OH)_2Si_4O_{10}$	1,57	2,74	3,65	0,91	Landolt Börnstein (1955)
Gillespite $BaFeSi_4O_{10}$	1,59	2,78	3,60	0,90	Structure Rep. vol. 9.
Antigorite $Mg_6(OH)_8Si_4O_{10}$	1,67	2,94	3,40	0,85	Structure Rep. vol. 13.
Tectosilicates*		Complex anions $AlSi_3O_8^{1-}$ and $Al_2Si_2O_8^{2-}$			
α-Celsian $BaAl_2Si_2O_8$	1,66	2,92	3,06	0,76	Structure Rep. vol. 13.
Orthoclase $KAlSi_3O_8$	1,64	2,88	2,92	0,73	Structure Rep. vol. 13.
Sanidine $KAlSi_3O_8$	1,66	2,93	2,90	0,72	Taylor (1933)
Albite $NaAlSi_3O_8$	1,67	2,94	2,90	0,72	Taylor and Derbyshire (1934)
β-Tridymite	1,54	2,68		0,74	Landolt—Börnstein (1955)
β-Cristobalite	1,57	2,74		0,73	Nieuwenkamp (1935), Bragg (1930), Tertsch (1941)
α-Cristobalite	1,59	2.78		0,71	Tertsch (1941)
α-Quartz	1,60	2,80		0,71	Machatschki 1936, Bragg (1930), Tertsch (1941)
β-Quartz	1,61	2,82		0,71	Tertsch (1941), Pei Hsiu Wei (1933)

* In the case of the muscovite and in that of the tectosilicates, computing the complexanionic potentials as well as the $\psi/(Si,Al)O_4$ values also the Al substitution is taken into consideration.

b) Sorosilicates

In the sorosilicates two SiO_4 tetrahedra are linked together by one shared oxygen to $Si_2O_7{}^{6-}$ silicate anion. From the potential value of 1,40 the portion for one oxygen is 0,35. Since two tetrahedra are linked from the twofold value of the SiO_4 anionic potential (1,40) is to be subtracted the potential portion for one oxygen. That is $2 \times 1,40 - 1 \times 0,35 = 2,45$. The value obtained is the anionic potential of $Si_2O_7{}^{6-}$ silicate anion. According to the basis started, however, the anionic potential, characteristic of single SiO_4 groups present in all of the different structures, is to be calculated. This value in the sorosilicates is $2,45/2 = 1,22$. *(Fig. 3)*

c) Cyclosilicates

Three SiO_4 tetrahedra form the ring characteristic of benitoite. The complex anion is $Si_3O_9{}^{6-}$. Here, therefore, the portion for three oxygens is to be subtracted from the threefold value of SiO_4 anionic potential, that is $3 \times 1,40 - 3 \times 0,35 = 3,15$. This value would be the anionic potential of the $Si_3O_9{}^{6-}$ anion and the corresponding ψ/SiO_4 is 1,05.

Six tetrahedra form the ring characteristic of the beryl. The complex silicate anion is $Si_6O_{18}{}^{12-}$. The ratio of $Si : O$ is $1 : 3$. From the sixfold value of the SiO_4 anionic potential the portion of potential value for six oxygens is to be subtracted, that is $6 \times 1,40 - 6 \times 0,35 = 6,30$. The value obtained can be considered as the potential of the $Si_6O_{18}{}^{12-}$ anion. From this value the potential characteristic of the single SiO_4 tetrahedron in cyclosilicates is 1,05. *(Fig. 4)*

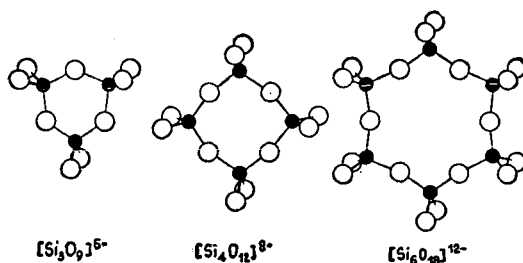$[Si_3O_9]^{6-}$ $[Si_4O_{12}]^{8-}$ $[Si_6O_{18}]^{12-}$

Fig. 4.

d) Inosilicates

In the structure of pyroxenes the SiO_4 tetrahedra form single-chains and the complex anion is $Si_2O_6{}^{4-}$ anion. Anyhow, even in the case of inosilicates characterized by single or double-chains or in that of the phyllosilicates characterized by sheets of linked SiO_4 tetrahedra, it is arbitrary to some extent, how great portion of these chains, bands or sheets consisting of linked tetrahedra are considered as complex silicate anions characteristic of the single structure types. So in the case of pyroxenes the $SiO_3{}^{2-}$ or the $Si_2O_6{}^{4-}$ or in the case of phyllosilicates

the $Si_2O_5{}^{2-}$ or the $Si_4O_{10}{}^{4-}$ complexes may also be considered as anions characteristic of the given structures although in all structures mentioned the real complex anions are the SiO_4 tetrahedra able to manifold linkage.

Also from this point of view seems to be justified to consider rather the SiO_4 tetrahedron present in all the various structures and its potential calculation, respectively, as the basis of anionic potential computations than the silicate anions being expressed in the chemical formulae and their potential calculations, respectively.

$$[Si_2O_6]^{4-} \qquad [Si_4O_{11}]^{6-}$$
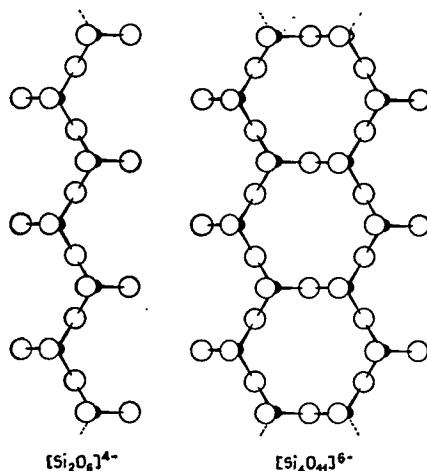
Fig. 5.

The ψ/SiO_4 in the pyroxenes is also 1,05 as the ratio of Si : O is the same as in the case of cyclosilicates that is 1 : 3.

In the structure of amphiboles the characteristic silicate anion formed by linkage of two single chains is $Si_4O_{11}{}^{6-}$. The anionic potential of this anion would be $4 \times 1,40 - 5 \times 0,35 = 3,85$, whereas the ψ/SiO_4 potential characteristic of amphiboles is 0,96. (Fig. 5)

e) Phyllosilicates

In the lattice of phyllosilicates the silicon tetrahedra are linked together to sheets and the characteristic complex silicate anion $Si_4O_{10}{}^{4-}$. Its potential value is $4 \times 1,40 - 6 \times 0,35 = 3,50$ and the ψ/SiO_4 potential is 0,87. (Fig. 6)

f) Tectosilicates

The SiO_4 tetrahedra form a framework lattice and the Si : O ratio is 1 : 2, that is the characteristic radical would be $SiO_2{}^0$ (the structure of the SiO_2 varieties). In the structure of tectosilicates the Si^{4+} ion can be replaced by Al^{3+} ion in different proportions. Such anions are $AlSiO_4{}^{1-}$, $AlSi_2O_6{}^{1-}$, $AlSi_3O_8{}^{1-}$, $Al_2Si_2O_8{}^{2-}$. The Si + Al : O ratio in these anions is 1 : 2. Consequently in general — for the time being apart from the

presence of AlO_4 tetrahedra — merely the $Si:O$ ratio taking into calculation, the potential would be $1 \times 1,40 - 2 \times 0,35 = 0,70$. This value is essentially the potential reckoned for one tetrahedron of the SiO_2^0 complex and may also be considered as the compound-potential of the SiO_2. *Szádeczky-Kardoss* (1954) on the basis of other considerations also assumes that the compound-potential of the quartz would possibly be 0,69.
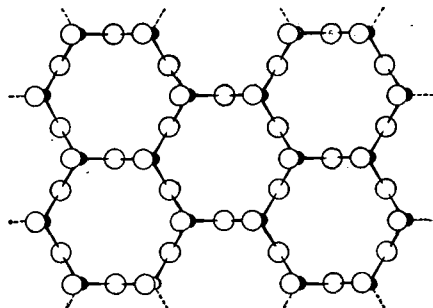
$$(Si_4O_{10})^{4-}$$

Fig. 6.

Calculating the ψ/SiO_4 potentials in the case of tectosilicates, must be taken into consideration the presence of AlO_4 tetrahedra, the type of linkage as well as the ratio of SiO_4 and AlO_4 tetrahedra. The mode of calculations demonstrated on $AlSiO_4^{1-}$ is as follows:

According to the data of Table 9 the average $Al-O$ distance in the AlO_4 tetrahedra is 1,70 Å, the average of the anionic radius is 2,92 Å and consequently the anionic potential is 1,70. (In the potential value of 1,70 the linkage of the AlO_4 tetrahedra is not taken into account.)

The portion for one oxygen from the anionic potential value of AlO_4 tetrahedron is 0,42, whereas that of in the SiO_4 tetrahedron is 0,35. If the ratio of the SiO_4 and AlO_4 tetrahedra in the structure is $1:1$, the anionic potential of the $AlSiO_4^{1-}$ complex anion may be computed as follows:

$$\psi/AlO_4 = 1 \times 1,70 - 2 \times 0,42 = 0,86$$
$$\psi/SiO_4 = 1 \times 1,40 - 2 \times 0,35 = 0,70.$$

Therefore the potential of the $AlSiO_4^{1-}$ anion is $0,86 + 0,70 = 1,56$ and the $\psi/(Si,Al)O_4$ potential characteristic of one tetrahedron of this structure is 0,78.

Similarly can be calculated the potential value of other complex silicate anions with Al substitution and divided this value by the number of $(Si + Al)$ atoms, the $\psi/(Si,Al)O_4$ potential characteristic of one tetrahedron of the given structure will be obtained.

The data of Tables 8 and 10 clearly show the decreasing tendency of the ψ/SiO_4 potentials relating to the single SiO_4 tetrahedra from the nesosilicates to the tectosilicates. The decrease of the ψ/SiO_4 potentials with increasing polymerization is illustrated in Fig. 7.

Table 9.

The change of the Al—O distance as well as that of the radius and anionic potential of the AlO_4^{5-} anion in some silicates.

Mineral	Al—O distance	r_{AlO_4}	ψ_{AlO_4}	References
α-carnegieite $NaAlSiO_4$	1,65	2,82	1,77	Barth and Posnjak (1935)
Scapolite 3 $NaAlSi_3O_8 . NaCl$	1,65	2,82	1,77	Schiebold and Seumel (1932)
Nosean $Na_8Al_6Si_6O_{24} . SO_4$	1,66	2,84	1,76	Barth (1933)
Sanidine $KAlSi_3O_8$	1,67	2,86	1,74	Taylor (1933)
Albite $NaAlSi_3O_8$	1,67	2,86	1,74	Taylor (1934)
Eucryptite $LiAlSiO_4$	1,69	2,90	1,72	Structure Rep. vol. 12.
Sillimanite Al_2SiO_5	1,70	2,92	1,71	Bragg (1930), Hey and Taylor (1931)
Haüynite $Na_6Ca_2Al_6Si_6O_{24}(SO_4)_2$	1,71	2,94	1,70	Bubeck and Machatschki 1935
Sodalite $Na_8Al_6Si_6O_{24} . Cl_2$	1,74	3.00	1,66	Barth (1933)
Zunyite $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$	1,74	3,00	1,66	Pauling (1933)
Cordierite $Mg_2Al_4Si_5O_{18}$	1,78	3,08	1,62	Structure Rep. vol. 9.
Average	1,70	2,92	1,71	

Table 10.

The variation of the ψ/SiO_4 potential depending on the degree of polymerization.

Si : O ratio	Structure type	Complex anion	$\psi_{complex}$	ψ/SiO_4 calculated on the basis of the average Si—O distances of 1,62 Å	of the actual Si—O distances within the single groups
1 : 4	Nesosilicates	SiO_4^{4-}	1,40	1,40	1,35
1 : 3,5	Sorosilicates	$Si_2O_7^{6-}$	2,44	1,22	1,20
1 : 3	Cyclosilicates	$Si_3O_9^{6-}$	3,15	1,05	1,07
		$Si_6O_{18}^{'2-}$	6,30		
1 : 3	Inosilicates — Pyroxenes	$Si_2O_6^{4-}$	2,10	1,05	1,05
1 : 2,75	Amphiboles	$Si_4O_{11}^{6-}$	3,85	0,96	0,96
1 : 2,5	Phyllosilicates	$Si_4O_{10}^{4 .}$	3,50	0,87	0,89
1 : 2	Tectosilicates	$Al_2Si_2O_8^{2-}$	3,20	0,80	0.76
	and quartz, resp.	$AlSi_3O_8^{1-}$	2,96	0,74	0,72
		$Si_4O_8^0$	2,80	0,70	0,72

In Fig. 7 the ψ/SiO_4 potentials of various types of silicates represented by the points found on the full line are calculated from the average (1,62 Å) of the Si—O distances measured in the different silicates, whereas the circles, partly close to the line, represents the ψ/SiO_4 potentials computed on the basis of the average of the Si—O distances determined in the single groups of the silicates.
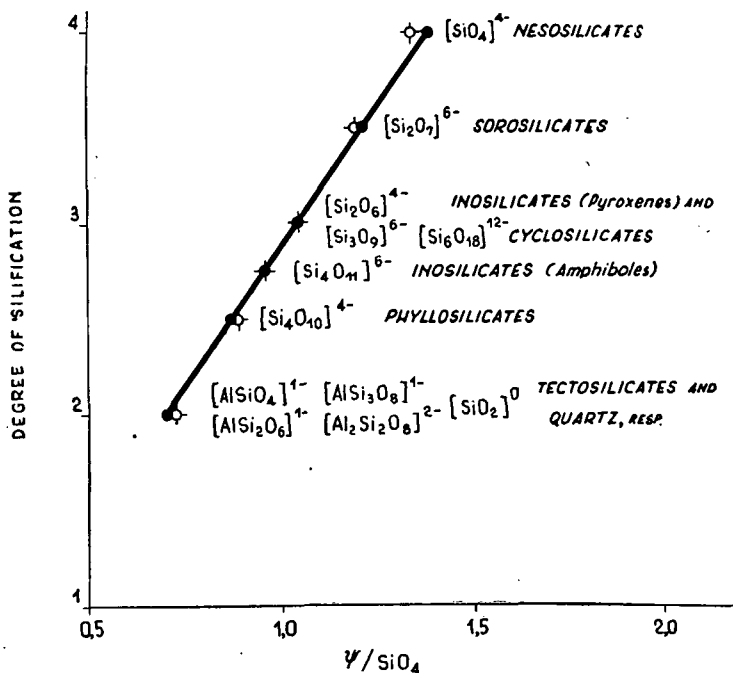

Fig. 7. The change ot the ψ/SiO_1 potentials depending on the degree of the silification

It was assumed also by *Szádeczky-Kardoss* (1954) that in the silicates the potential value presumably decreases by the linkage of the tetrahedra relating to the 1,38 potential value given for the separate SiO_4 anion, as it is shown by his following statements: „Bei weiterer Verknüpfung der SiO_4-Tetraeder setzt sich die Abnahme des Ionenpotentials weiter fort. So ist z. B. das Ionenpotential der durch die Assoziation von zwei SiO_4-Tetraedern zustande gekommenen $(Si_2O_7)^{6-}$-Gruppe offenbar kleiner als 1,38, das von noch grösseren Gruppe allmählich noch kleiner.” Thus, in *Szádeczky-Kardoss's* opinion the decrease of the potential values may be expected in the relation of the different complex silicate anions, that is, in that of $Si_2O_7^{6-}$, $Si_2O_6^{4-}$, $Si_4O_{11}^{6-}$, $Si_4O_{10}^{4-}$ silicate anions.

The correctness of *Szádeczky-Kardoss's* supposition is proved also

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by the results of the present work, that is, the complex anionic potential decrease by increasing degree of linkage, this decrease, however, is revealed in the decrease of the ψ/SiO_4 potentials relating to the single SiO_4 tetrahedron.

Summarizing it can be stated that the change of the anionic potential of the SiO_4 depending on the degree of silification corresponds to the conclusions of infrared spectra of silicates and the correctness of the assumption relating to the variability of the SiO_4 anionic potentials expressed in the ψ/SiO_4 potentials seems to be supported by the results of exact physical examinations. The $SiO_4{}^{4-}$ complex anionic potential became more expressive by introducing of the ψ/SiO_4 values and thereby a greater possibility of their application is obtained in different fields as for example the calculation of the compound-potentials of the silicates, the interpretation of the sequence of magmatic crystallization as well as the examination of the stability relations of the silicates on the basis of the complex anionic and the compound-potentials, respectively.

5. THE VARIABILITY OF THE $BO_3{}^{3-}$ COMPLEX ANIONIC POTENTIAL AND THE STRUCTURAL PECULIARITIES OF THE BORATES

The connection between the anionic potential of $BO_3{}^{3-}$ ion and the structures characteristic of borates may be briefly discussed as follows.

In all types of borates the characteristic anion is the $BO_3{}^{3-}$ anion capable of being linked together in different ways. There are also among the borates that compounds characterized by independent, separate $BO_3{}^{3-}$ groups and such compounds wherein two $BO_3{}^{3-}$ groups are linked together to $B_2O_5{}^{4-}$ anion. The $BO_3{}^{3-}$ groups can be linked forming rings or chains too.

Bearing in mind the data of Table 11 it can be stated that also the potential of the $BO_3{}^{3-}$ anion changes — similar to the of the other complex anions — depending upon the change of the ionic distances and on the other hand the ψ/BO_3 value changes by the degree of polymerization of the BO_3 groups. The ψ/BO_3 potential also in the case of borates shows a decreasing tendency by the increasing degree of polymerization as it could be seen in the silicates. It would be worthwhile to know what connection could be established between the change of the anionic potential of $BO_3{}^{3-}$ depending on the polymerization and the results of the infrared sprectroscopical examinations referring to the borates of different structural types.

It is to be mentioned, although the possibility of the linkage of the complex anions is characteristic firstly of the silicates and borates, sometimes also the linkage of some complex anions in general characteristic of anisodesmic structures can be established. Thus the structures of BPO_4 and $BAsO_4$, respectively, are closely related to that of the α-cristobalite. In the case of $AlPO_4$ having lattice of SiO_2-type all the modifications of SiO_2 were established.

In such cases calculating the potential of the given anion — according to the calculation-method given for the silicates — beside the change of ionic distances, the degree of polymerization must be also taken into consideration.

Table 11.

The change of the complex anionic potential of BO_3^{3-} anion depending on the change of the ionic distance and on the degree of polymerization.

Compound	B—O distance	Complex anion	r_{BO_3}	$\psi_{complex}$	ψ/BO_3	References
$ScBO_3$	1,25	BO_3^{3-}	2,29	1,31	1,31	Leutwein and Doerffel (1956)
Be_2BO_3OH Hambergite	1,35		2,49	1,20	1,20	Zachariasen (1931)
H_3BO_3 Sassolite	1,36		2,51	1,19	1,19	Zachariasen (1934) Landolt—Börnstein (1955)
$Mg_3(BO_3)_2$ Kotoite	1,38		2,55	1,17	1,17	Structure Rep. vol. 11.
$(Mg.Mn^{II})Mn^{III}O_2BO_3$ Pinakiolite	1,40		2,59	1,15	1,15	Structure Rep. vol. 13.
$(Mg,Fe^{II})Fe^{III}O_2BO_3$ Ludwigite	1,40		2,59	1,15	1,15	Structure Rep. vol. 13.
$Mg_3(F,OH)_3BO_3$ Fluoborite	1,44		2,67	1,12	1,12	Structure Rep. vol. 13.
$Ca_2B_2O_5$	1,29	$B_2O_5^{4-}$	2,37	2,10	1,05	Structure Rep. vol. 13.
CaB_2O_4	1,36	$B_2O_4^{2-}$	2,51	1,60	0,80	Zachariasen and Ziegler 1933
$K_3B_3O_6$	1,36	$B_3O_6^{3-}$	2,51	2,38	0,79	Fang (1938)
$Na_3B_3O_6$	1,36		2,51	2,38	0,79	Fang (1938)

6. COMPLEX ANIONS IN GEOMETRICAL AND IN PHYSICAL SENSE IN CRYSTALS

It has been pointed out that owing to the variability of the complex anionic potentials they must be always computed bearing in mind the actual conditions in the lattice in question. The calculation with the actual ionic distances, however, means merely the one part of the circumstances valid in lattice to be taken into consideration. Non the less is essential the establishment — especially from the point of view of the calculation of the compound potential — whether the complex anion expressed in the chemical formula in the lattice of the crystals exists as real complex anion in physical sense or in the lattice rather geometrical groups exist merely, that is, whether the given structure is an anisodesmic or meso-desmic structure with discrete complex anions or simple coordination lattice without formation of radicals.

It is known this question can not be decided but on the basis of the chemical formula.

For example in the lattice of the spinel (Al_2MgO_4) the presence of the loose complex anion MgO_4^{6-} was yet supposed by *Goldschmidt*. Studying, however, the structure of the spinel it has been proved by

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Machatschki (1931) that in the lattice $MgO_4{}^{6-}$ complex anion can not exist, since: „Die geringere Raumbeanspruchung und höhere Wertigkeit des Ions Al^{3+} gegenüber dem Ion Mg^{2+} macht eine kräftige Kontrapolarisation unter Bildung eines neuen Radikals MgO_4 im Gitter ohnehin unwarscheinlich."

Leutwein and *Doerffel* (1956) have computed the Fersman's EK (energy coefficient) values of different complex anions from the following equation:

$$EK = \frac{128 \cdot z^2}{r^{3/2}},$$

where z means the charge and r the radius of the complex anion. Moreover they have computed the EK values of the $NbO_3{}^{1-}$, $TiO_3{}^{2-}$, $JO_3{}^{1-}$ „complex anions" expressed in the chemical formulae of the corresponding compounds, that is, in that of the $NaNbO_3$, $CaTiO_3$ and KJO_3. According to these formulae momentarily the presence of the anions mentioned in the lattice may be assumed, this assumption, however, does not correspond to the real conditions in the lattice. Namely, in the lattices of the compounds enumerated, the presence of such complex anions can not be established, since in these lattices such groups which would be distinguished from the other components of the lattice as discrete units owing to the strength and character of the bonding within the groups, do not exist. Each compound mentioned, have perowskite type structure, that is, they have simple coordination structure and not anisodesmic one. In the lattice of perowskite ($CaTiO_3$) the Ti^{4+} ion, in the lattice of $NaNbO_3$ the Nb^{5+} ion and in the lattice of KJO_3 the J^{7+} ion is surrounded by six oxygen ions, that is in the lattices of this type TiO_6, NbO_6, JO_6 octahedral groups exist, which, however, can not be considered as complex anions in physical sense.

As among the compounds of ABO_3-type neither in the structure of ilmenite ($FeTiO_3$) type nor in that of the perowskite ($CaTiO_3$) type BO_3 complex anions do not exist, so, it is not quite correct to mention the compounds of such type as titanates, zincates, zirconates, iodates etc., as it has been emphasized also by *Hiller* (1952).

Similarly the $TlJO_3$ possesses structure of perowskite type that is in its lattice merely JO_6 octahedral groups may be distinguished but not $JO_3{}^{1-}$ complex anions, while in the lattice of $NaJO_3$ on the basis of investigations of *Náray-Szabó* and *Neugebauer* (1947) the presence of the $JO_3{}^{1-}$ complex anion can be supposed. The difference between the formal and real complex anion in the two compounds mentioned above is expressed also by the difference between the ionic distances within the complexes, as the J—O distance in the $TlJO_3$ is 2,22 Å whereas that of in the $NaJO_3$ 1,80—1,83 Å.

In the lattice of Li_2WO_4 isomorphous with phenacite the presence of LiO_4 as complex anion similarly can not be assumed. *Schaefer, Matossi* and *Wirtz* (1934) as well as *Matossi* and *Krüger* (1936) studying the infrared reflection spectra of the silicates and the compounds above-mentioned stated: „...dass zwar BeO_4-Tetraeder (Phenacit) und

BO$_4$-Tetraeder (Danburit) als mit den SiO$_4$-Gruppen gleichberechtigte physikalische Baugruppen in den Silikaten existieren, nicht aber LiO$_4$-Tetraeder im Wolframat, denen hier nur geometrische Bedeutung zukäme." In the spectra of the corresponding compounds it was possible to point out reflection bands characteristic and attributable to SiO$_4$-, BeO$_4$-, BO$_4$-tetrahedra, respectively, but the band expected for the LiO$_4$ tetrahedron was missing.

Leutwein and *Doerffel* (1956) in their paper computed also the EK value of the SiO$_3{}^{2-}$ complex anion supposed in the lattice of MgSiO$_3$. However, such an assumption seems to be more probable that also in the lattice of this compound essentially SiO$_4$ tetrahedra exist similarly to the lattices of the different silicates and the formula above-mentioned with the apparent SiO$_3{}^{2-}$ complex anion is obtained only due to the linkage of these tetrahedra. *Schaefer, Matossi* and *Wirtz* (1934) mention the previous examinations of *Schaefer* and *Schubert* intending to establish — in analogy with carbonates — the existence of independent SiO$_3{}^{2-}$ groups in the lattice of the metasilicates on the basis of their infrared spectra. The existence of the SiO$_3$ groups was not to be proved by their results. The complicated structure of the silicates at that time was yet not fully known, but in connection with the structure of the quartz, however, was acquainted that the infrared spectra of quartz can not be correlated with the existence of SiO$_2$ groups. The authors mentioned final concluded that: „Die scheinbare SiO$_3$-Gruppe der Metasilikate durch ganz verschiedene Anordnungen von SiO$_4$-Tetraedern erzeugt werden kann." Similarly stated *Kujumzelis* (1938) examining the correlations between the vibrations of XO$_3$ ions and their structure by Raman-spectra: „Der Einbau der SiO$_4$ Tetraeder ins Gitter der Metakieselsäurepolymere geschieht in so verschiedener Weise, dass die SiO$_3$-Gruppe als einfaches Ion nicht ohne Zweifel betrachtet werden kann." These statements are supported by *Fyfe's* (1954) examinations relating to the problem of bond type discussing why there is no SiO$_3{}^{2-}$ group corresponding to the CO$_3{}^{2-}$ groups, and conversely no CO$_4{}^{4-}$ group corresponding to SiO$_4{}^{4-}$.

What possibilities of error is implied without taking into consideration the peculiarities of the structure in question, without distinguishing between formal, only geometrical groups and the real complex anions, especially tending to compute tha lattice energy or the compound potential?

Calculating the compound potential of the spinel assuming in the lattice the real existence of the apparent MgO$_4{}^{6-}$ complex anion in the chemical formula, then

$$\psi_{Al_2MgO_4} = \frac{2 \cdot \psi_{Al} + 1 \cdot \psi_{MgO}}{3} = \frac{2 \cdot 5{,}88 + 1 \cdot 1{,}75}{3} = 4{,}5$$

whereas considering the spinel according to *Machatschki* as simple coordination lattice without complex anion as it was considered also by *Szádeczky-Kardoss* at the computation of the compound potential, then

$$\psi_{Al_2MgO_4} = \frac{2 \cdot \psi_{Al} + 1 \cdot \psi_{Mg} + 4 \cdot \psi_O}{7} = \frac{2 \cdot 5{,}88 + 1 \cdot 3{,}22 + 4 \cdot 1{,}51}{7} = 3{,}0$$

It has been previously mentioned that *Leutwein* and *Doerffel* have computed EK values for NbO_3^{1-}, JO_3^{1-}, TiO_3^{2-} complex anions too, although the structures wherein they assumed the presence of the complex anions mentioned, are simple coordination structures without complex anions. It is questionable, whether the EK value calculated for a complex anion, in fact not found in the lattice, may be considered as real and characteristic value and particularly it is doubtful, whether the compound can be characterized accurately by the lattice energy computed from such EK values?

Thus, supposing the existence of the TiO_3^{2-} anion in the perowskite and calculating the lattice energy by addition of the corresponding EK values, it would be obtained

$$U'_{CaTiO_3} = EK_{Ca} + EK_{TiO_3} = 572 \ kg. \ cal./mol.,$$

that is the energy needed to decompose the compound into Ca^{2+} and TiO_3^{2-} ions if in the $CaTiO_3$ would be really exist the TiO_3^{2-} anion. Calculating on this basis the complex anionic potential, it would be 0,62, whereas the compound potential of the $CaTiO_3$ 1,25.

Correct results, however, will be obtained only taking into consideration the real conditions in the lattice, that is, the perowskite must be considered as simple coordination structure without any complex anion with three sorts of ions. Accordingly the lattice energy would be

$$U_{CaTiO_3} = EK_{Ca} + EK_{Ti} + 3 \ EK_O = 3647 \ kg.cal./mol.,$$

and the calculated compound potential 2,53.

These two examples seem to be enough to show how essential is, from the point of view of calculation of both the lattice energy and the compound potential, to take into consideration the really existing conditions in the lattice.

Summarizing the above-mentioned, it can be stated that only after studying the structures of the different compounds and the bonding character within the complex anions, supposed firstly merely on the basis of the chemical formula of the compound can be decided, whether this group can be considered as a real complex anion or it is only a geometrical group without the characteristics of a complex anion.

When the existence of complex anion is proved in the compound, it can be stated also from the structure investigations, whether the complex anion expressed formally in the chemical formula corresponds to the complex anion existing really in the lattice.

The emphasize of these aspects seems to be no less important from the point of view of the computations of lattice energy or compound potential than to take into consideration the change, the variability of the ionic distances and the complex anionic potentials, respectively.

SUMMARY

1. The complex anionic potentials introduced by *Szádeczky-Kardoss* are not constant values nor in the case of the same complex anion. The ionic distances within the same complex anion in the different compounds may be varied depending upon the polarizing force of the central cation and the contrapolarizing effect as well as the coordination number of the neighbouring cations. Since the change of the ionic distances within the complex anion is associated with the change of the radius of the complex anion, consequently, the complex anionic potential may be varied from compound to compound also in the case of the same anion. This possible change depends primarily on the change of the ionic distances in the anisodesmic structures. In the mesodesmic structures like in the silicates and borates beside the change of the anionic potentials due to the change of the ionic distances, yet in consequence of its numerical value as well as of its geochemical significance the variation of the complex anionic potential depending on the degree of polymerization proves to be considerably more significant.

To take into account the variability of the complex anionic potentials is especially essential calculating the compound potentials.

2. The most distinctive feature of the silicates is partly the presence of the SiO_4^{4-} group in all the silicates of different structure types and partly the manifold linkage of these tetrahedral groups. The behaviour and properties of the SiO_4 anion, that is, that of the fundamental structure element of the silicates vary depending upon the degree of polymerization of the SiO_4 tetrahedra as it is proved either by the results of infrared spectroscopical investigations of silicates or by the statements of other examinations based on thermochemical data. The experimental results and the theoretical considerations equally show that the peculiarities of the SiO_4 tetrahedra change depending on the degree of polymerization from the nesosilicates toward the tectosilicates. To characterize these changes the ψ/SiO_4 potentials were introduced as the expression of the variable complex anionic potential relating to the SiO_4 tetrahedron equally present in all silicates with variable properties. These values are characteristic of the single groups of silicates and by these values the influence on the change of the complex anionic potential exerted by both the ionic distances and the degree of polymerization is expressed. The ψ/SiO_4 potentials can be simply calculated taking into account the ionic distances as well as the degree of silification. The ψ/SiO_4 potentials decrease from the nesosilicates toward the tectosilicates.

3. In the mesodesmic borates can be similarly pointed out the change of the complex anionic potential depending partly on the change of ionic distances and partly on the degreee of polymerization of BO_3^{3-} groups. The value of ψ/BO_3 potentials decreases as the degree of polymerization increases.

4. The compound potential can be calculated from the ionic potential of the cations and the anionic potential of the complex anion taking into account also the number of ions in the molecule according to the given formula. The lattice energy may be calculated from the Fersman's EK

values by simply adding these values. It is shown that from the point of view of calculation of both the compound potentials and the lattice energies (from EK values of the cation and complex anion) is essential to decide whether the group — which seems occasionally to be complex anion on the basis of chemical formula of the compound in question — can be considered as real complex anion in physical sense also in the crystal lattice of the compound or it is only a geometrical group without the characteristics of a complex anion.

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

Part II. Remarks to the calculation of the radii and anionic potentials of the complex oxyanions

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1. INTRODUCTION

The complex anionic potential according to *Szádeczky-Kardoss* (1954) is the quotient of the charge and the radius of the complex anion and may be considered as a value characteristic of the complex anion as a whole.

Now the question may arise what distance, given in Å units, may be considered as the radius of the triangular or tetrahedral oxyanions. Namely, the complex anionic radii computed by *Fersman* and used by *Saukov* (1953) and by *Szádeczky-Kardoss* (1954) are computed rather by simple addition of the ionic radii of central cation and oxygen. The ionic distance within the complex anion may be changed depending on the polarizing force of the central cation and the contrapolarizing effect of the neighbouring cation as well as on its coordination number. This possible change of the ionic distances is not taken into consideration calculating the complex anionic radii on the basis of simple ionic model.

Considering the different complex oxyanions as elements of crystal lattices of different solid compounds of anisodesmic and mesodesmic structure, it has been pointed out by the author *(Grasselly,* 1958, 1959a) that the radius of the complex anions due to the factors above-mentioned may be changed from compound to compound also in the case of the same complex anion and therefore the anionic potentials are to be considered as variable values.

In connection with the calculation of the radius as well as the potential of the complex anions a further question may also arise the satisfactorily solution of which, in our opinion, implies the possibility of the further refinement of the calculation method of the complex anionic potential.

The problem and the way of the solution which seems to be practicable at least as approximation, may be discussed as follows.

2. THE MEANING OF THE ANIONIC POTENTIAL
FROM ELECTROSTATIC VIEWPOINT

The ionic potential of the cations from the electrostatic viewpoint is
·considered by *Mason* (1952) as a measure of the charge density on the
.surface of the cation. Similarly *Goldschmidt* (1954) in his book considers
the quotient charge/radius, that is the ionic potential, as a measure of
the field strength at the surface of the polarizing ion. It is to be noted,
however, that the z/r is not the quite correct expression for the charge
·density at the surface of the cation as it would be correctly given by the
·expression $\dfrac{z \cdot e}{4 \pi r^2}$. The increase of the numerical value of the ionic poten-
tials, however, goes together with the increase of the values computed
.from the correct expression of the .charge density if for example the
charge increases at constant radius, though the rate of the increase of the
·values of these two kinds differs.

Apart from these necessary remarks, howewer, the ionic potentials
.may be considered at least as a qualitative measure of the charge density
·on the surface of the cation. Under constant charge the larger is the ra-
·dius the lower will be the ionic potential that essentially means the de-
·crease of the charge density at the surface.

Analogously the anionic potential of the simple anions — considering
them also as spheres apart from the possible deformation — introduced
by *Szádeczky-Kardos* (1954) may be considered as a qualitative measure
·of the density of the negative charge at the surface of the anion.

3. THE CALCULATION METHOD PROPOSED FOR THE DETERMINATION
OF THE RADIUS OF NON-SPHERICAL COMPLEX OXYANIONS

As it has been already mentioned, *Szádeczky-Kardoss* has computed
the complex anionic potentials in the same manner as the potential of the
·cations, i. e., as the quotient of the charge and „radius". In practice it is
customary to speak about radii of complex anions and to calculate with
these values too and this· consideration implies that these complex anions
.are considered to be spherical. Now the question arises, whether the non-
:spherical tetrahedral or triangular oxyanions may be considered as rigid
spheres and hence it may be calculated with their „radius", or not?

On the one hand, it is a fact that these, essentially nonspherical, com-
plex ions may be considered only in that case as rigid spheres when in the
lattice the rotation of these complex ions may occur, consequently show-
.ing in statistical average a spherical symmetry. The fact of the rotation
of complex ions in crystals especially at higher temperatures is pointed
out by several authors. For example, in the lattice of NH_4NO_3 (structure
type: CsCl) stable over 125° C both the NH_4^+ and the NO_3^- groups ro-
tate. The radius of the rotation sphere corresponding to the NH_4^+ group
is 1,46 Å, whereas that of corresponding to the NO_3^- group is 2,35

On the other hand, *Goldschmidt* (1954) dealing with the ionization
potential as a measure of polarizing force of ions mentions that the non-

spherical complex ions as the triangular ions BO_3^{3-}, CO_3^{2-}, NO_3^{1-} or the tetrahedral ions like SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^{1-} can be considered to be rigid spheres, with a fair degree of approximation if their internal bonds give them a fair degree of rigidity, that is, these internal bonds within these complex anions are strong in comparison with the electrical forces exerted by neighbouring cations.

The radius of the complex anion equals $2a - r_c$, where a is the ionic distance measured roentgenographically and r_c is the radius of the central cation. The distance, considered as the radius of the complex anion, essentially is the radius of the sphere circumscribed around the tetrahedron.

Still an other question is, whether the complex anion would be rightly represented by the sphere of radius $2a - r_c$ and thus would be accurately characterized by the complex anionic potential calculated with this value or it would be better to substitute hypothetically the complex anion with an other sphere, the radius of which differs from that mentioned above.

Should the *Mason*'s opinion be applied to the complex anions too, i. e., the complex anionic potential would be considered as a qualitative measure of the density of the negative charge at the surface of the complex anions considered as spheres, it seems to be expedient to calculate with such a radius, to substitute the complex anion with such a sphere, the surface of which is close to the effective surface of the complex anion. On the other hand, also the importance of volume relationship in the lattice of crystals is well known.

Therefore, it seems to be expedient to substitute hypothetically the complex anion with such a sphere, the volume and surface of which mostly approach that of the complex anion.

This consideration can be presented by showing the possibilities of the calculation-method of the anionic potential of SO_4^{2-} anion.
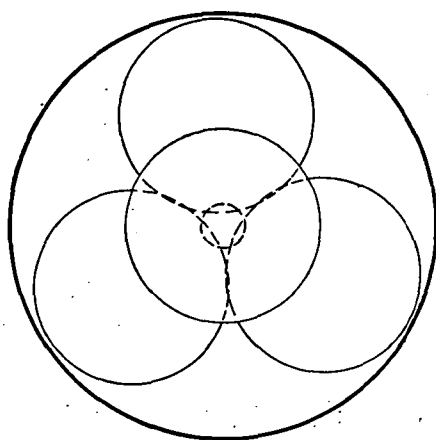

Fig. 1

a) In the lattice of anhydrite, according to *Wooster* (1936), the distance of S—O is 1,55 Å and that of O—O is 2,50 Å. In general the radius of the complex ion SO_4^{2-} equals $r = 2 \times 1,55 - 0,28 = 2,82$ Å. Calculating the complex anionic potential too, it will be 0,70. In *Mason*'s opinion this value can be considered as a measure of the density of negative charge at the surface of the sphere to be circumscribed around the tetrahedron and having a radius of 2,82 Å. In Fig. 1, the full line circle represents this sphere. It is observable that this sphere includes to a significant extent such a space too actually not engaged by the SO_4 tetrahedron.

b) Fig. 2 demonstrates within the SO_4 tetrahedron, the tetrahedron whose edge equals with the distance of O—O measured roentgenographically, that is with 2,5 Å. In the Fig. 2, the circle drawn with full line represents the sphere having the same volume as the tetrahedron of edge 2,5 Å. The radius of the sphere is 0,76 Å and the complex anionic potential calculated from this value is 2,6. It is obvious that the complex anion can not be symbolized by this sphere and the radius of this sphere can not accepted as the radius of the complex anion.
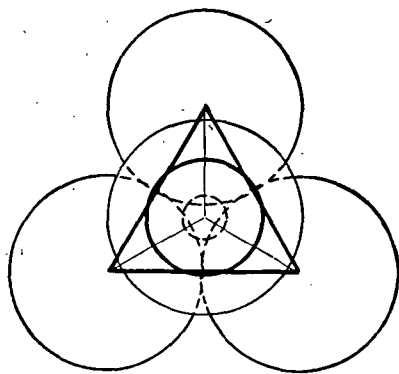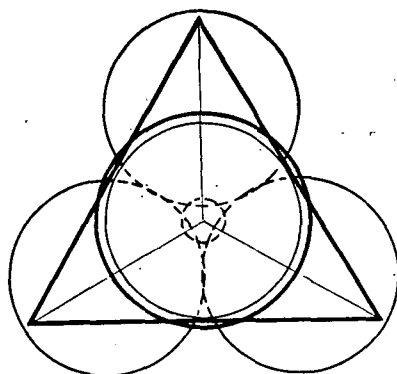
Fig. 2   Fig. 3

c) Fig. 3 shows the tetrahedron wherein the distance between its centre and corner is 2,82 Å that is it equals with the radius of the SO_4 complex anion. The centre of the tetrahedron coincides with that of the central cation. The radius of the sphere having the same volume as this tetrahedron is 1,40 Å and the computed anionic potential from this value is 1,42. As it can be seen in Fig. 3, also this sphere is of less volume and surface than the SO_4 tetrahedron, therefore, tending to calculate the complex anionic potential, the SO_4 anion presumably can not be substituted by the sphere obtained in such manner.

d) So far it was examined how the spheres deduced in different way from data obtained from roentgenographic measurements can be related to the SO_4 complex anion regarding to their volume. Moreover, sketches of b) and c) demonstrate that the SO_4^{2-} complex anion can not be substituted by spheres obtained in the manner given under b) and c).

Intending to find the sphere probably most corresponding in its volume to that of the SO_4^{2-} complex ion, firstly the oxygen ions are to be drawn representing by circles, taking as distance between their centre the O—O distance roentgenographically determined. Then tangents will be drawn to these circles on the three sides adn the triangle so obtained is to be considered as a plate of the tetrahedron, the volume of which had to be calculated. Finally, the radius of the sphere identical in its volume to that of the tetrahedron constructed is to be calculated. The O—O distance in the present example is 2,5 Å. The radius of the sphere adequate in volume with the tetrahedron constructed as mentioned above is 2,12 Å and the complex anionic potential is 0,94.

In Table 1 are comprised the data referring to the surface, volume and radius relations of the spheres and tetrahedra, respectively, deduced in the manner given under a), b), c) and d).
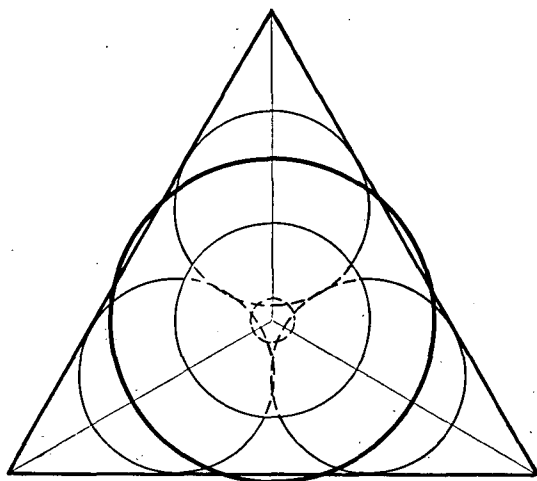
Fig. 4

To illustrate which of the different spheres characterized by the data given in Table 1 corresponds mostly to the SO_4^{2-} complex ion as to its volume and surface, let us make the following calculation of approximative character. The radius of the oxygen ions in SO_4 from the roentgenographic data may be taken as 1,27 Å, since the S—O distance is 1,55 Å and the Ahrens's radius of the S^{6+} ion corrected for four-coordination number is 0,28 Å. On this basis the volume of each oxygen ion considered as spheres, with radius 1,27 Å, amounts to 8,5 $Å^3$ and that of the four oxygen ions is 34 $Å^3$. The surface of the single oxygen ions, at the same radius value, will be 20 $Å^2$ and that of the four oxygen ions 80 $Å^2$, respectively.

As it can be seen the volume and surface values calculated for the SO_4^{2-} anion are close to that of the tetrahedron and of the sphere with equal volume, respectively, constructed in the manner, given under d),

especially taking into consideration that owing to the tetrahedral arrangement of the oxygen ions only a part of the whole surface of the oxygen ions can be effective from viewpoint of the bonding.

Consequently, owing to this conformity, it seems to be very presumable that the SO_4^{2-} ion is hypothetically to be substituted in the lattice by a sphere, the radius of which is determined in the way given under d) and that the complex anionic potential calculated with this radius would be presumably more characteristic of the anion than the anionic potential calculated in the so far manner, i. e., taking as radius of the complex anion that of the sphere to be circumscribed round the tetrahedral anion.

Table 1.

		a	b	c	d
Volume of the tetrahedron and the sphere	Å³	93,87	1,84	11,50	40,40
Surface of the tetrahedron	Å²	148,83	10,82	36,65	84,86
Surface of the sphere	Å²	99,89	7,16	24,62	56,42
Radius of the sphere	Å	2,82	0,76	1.40	2,12
Complex anionic potential		0,70	2,63	1,42	0,94

Table 2.

Anion	O—O distance Å	Compound	Radius	Anionic potential	References
BO_3^{3-}	2,35	Na₃B₃O₃	1,96	1,53	Ssu-Mien Fang (1938)
CO_3^{2-}	2,13	BaCO₃	1,81	1,10	Colby, La Coste (1935)
NO_3^{1-}	2,10	KNO₃	1,76	0.56	Edwards (1931)
SiO_4^{4-}	2,56	BaTiSi₃O₉	2,12	1,88	Zachariasen (1930)
	2,61	CaMgSi₂O₆	2,19	1,82	Bragg (1930)
	2,68	KAlSi₃O₈	2,24	1,78	Structure Rep. vol. 9.
AsO_4^{3-}	2,60	Ag₃AsO₄	2,20	1,36	Structure Rep. vol. 11.
	2,76	NaAlFAsO₄	2,30	1,30	Kokkoros (1939)
	2,85	BiAsO₄	2,32	1,29	Structure Rep. vol. 11.
SO_4^{2-}	2,50	CaSO₄	2,12	0,94	Wooster (1936)
CrO_4^{2-}	2,61	Na₂CrO₄	2,16	0,92	Miller (1936)
ClO_4^{1-}	2,51	NaClO₄	2,09	0,47	Braekken, Harang (1930)
JO_4^{1-}	2,67	NaJO₄	2,22	0,45	Hazlewood (1938)

Table 2 includes some of complex anionic radius values determined in the way given in this paper as well as the O—O distances on the basis of which the construction of the hypothetically spherical ion has taken place, the radius of which is considered as the radius of the complex anion. Similarly the new complex anionic potentials are denoted.

4. CONNECTION BETWEEN THE THERMOCHEMICAL RADII OF COMPLEX ANIONS AND THE RADII DETERMINED IN THE WAY PROPOSED IN THIS PAPER

The probability of the correctness of our assumption relating to the computation method of anionic radii proposed in this paper seems to be supported when comparing these values with the thermochemical radii computed by *Kapustinski*. The term of thermochemical radius is introduced by *Kapustinski* and in his opinion it means the radius of a hypothetically spherical ion which isoenergetically substitutes a given ion in the crystal lattice. As it can be seen this definition and our view, discussed above, expresses almost the same.

Table 3.

Anion	Radius used in general computed from equation: $R = 2a - r_c$ R	Thermochemical radius R'	Radius computed by the author R''	Ratio R'' : R'
BO_3^{3-}	2,50	1,91	1,96	1,02
CO_3^{2-}	2,40	1,85	1,81	0,97
NO_3^{1-}	2,34	1,89	1,76	0,93
AsO_4^{3-}	2,93	2,48	2,27	0,91
JO_4^{1-}	2,88	2,49	2,22	0,89
SiO_4^{4-}	2,90	2,40	2,18	0,90
CrO_4^{2-}	2,74	2,40	2,16	0,90
SO_4^{2-}	2,76	2,30	2,12	0,92
ClO_4^{1-}	2,91	2,36	2,09	0,88

In Table 3 the thermochemical radii and the radii graphically determined by the author on the basis of roentgenometric data are compared. The thermochemical radii used are taken from *Jazimirski*'s work (1956) dealing with the thermochemistry of complex compounds.

As it can be seen in Table 3, the radius values of the triangular complex oxyanions computed by the author are nearly the same as the correspondig thermochemical radii and in the case of the tetrahedral oxyanions our radius values are more close to the thermochemical radii than the radii used in general calculated on the basis of roentgenographic data from the equation: $R = 2a - r_c$.

The thermochemical radii can be computed according to *Kapustinski* as follows. Knowing the heats of formation of the ingredient ions in gaseous state of a given compound as well as the heat of formation of the crystallized compound, from these data, firstly the lattice energy of the compound is to be computed according to the following equation:

$$U_k = -\Delta H°_{ka} + \Delta H°_k + \Delta H°_a$$

where U_k means the lattice energy, $-\Delta H°_{ka}$, $-\Delta H°_k$ and $-\Delta H°_a$ are the heats of formation of the crystallized complex compound and that

of the cation and the anion, respectively. Then the value U_k obtained is to be substituted into the *Kapustinski*'s equation:

$$U_k = \frac{\Sigma_n \cdot z_1 \cdot z_2}{r_1 + r_2} \left(1 - \frac{0,345}{r_1 + r_2}\right),$$

where Σ_n means the number of the ingredient ions in the molecule, z_1 and z_2 the charges and r_1, r_2 the radii of the ions, respectively. Knowing the radius of the cation, the radius of the complex anion can be determined.

As it may be seen the computation method proposed by the author based only on roentgenometric data (on the O—O distances within the complex anions) gives nearly the same radius values for complex oxyanions as the method above-mentioned based on thermochemical data in the case of the triangular oxyanions and the new radius values in the case of tetrahedral oxyanions are very close to their thermochemical radii and the quotient of these two values are nearly constant, $0,9 \pm 0,02$.

In our opinion, during the thorough investigations in progress concerning the connections afore-said, this conformity may offer partly the possibility of a calculation into the opposite direction, i. e., of the calculation of some thermochemical data from these radius values determined graphically from roentgenometric data and partly the possibility of the further refinement of the complex anionic potential calculations and finally it will be also possible to find connections between the complex anionic potentials and thermochemical data.

SUMMARY

The radius of the complex anions in general as a rule is calculated on the basis of roentgenographically measured data (central cation — oxygen distance) from the following equation: $R = 2a - r_c$, where a means the distance measured and r_c the radius of the central cation. This is essentially the radius of the sphere to be circumscribed round the tetrahedral anion. The complex anionic potential is given by the quotient of its charge and radius and may be considered as a qualitative measure of the charge density at the surface of the anion, however, from crystallochemical viewpoint, from the viewpoint of diadochy, substitution of complex anions also the volume relations are essential, therefore, a non-spherical complex anion is probably hypothetically to be substituted in the crystal lattice with such a sphere, the surface and volume of which are closest to that of the complex anion.

It is proposed a graphic method based on roentgenographically measured O—O distance within the complex anion to construct the sphere whereby the anion is to be substituted in the lattice, the radius of which sphere may be considered as the effective radius of the complex anion. These graphically determined „effective" anionic radii agree well with the thermochemical radii of anions introduced by Kapustinski and calculated from thermochemical data, from heats of formation and lattice energy.

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

Part III. The characterization of the relative stabilities of the complex silicate anions by the ψ/SiO_4 potentials

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1. INTRODUCTION

Dealing in general with the relative stabilities of the complex oxyanions *(Grasselly,* 1959a), it could be established that the increase of the stabilities expressed by the increasing electrostatic energy and energy constant values, respectively, by the ionic potential of the central cation within given limits may be characterized, however, to compare the stability relations of complexes the central ions of which belong to different periods or different groups of the periodic system, the complex anionic potentials proved to be rather generally applicable. In the case of the silicates the ionic potentials are not suitable all the more to use as the basis of comparison of the stability relations of the different silicate anions, since the central ion in all silicate anions is the same, that is the Si^{4+} ion with unchanged ionic potential. At the same time, however, verifying the variability of the complex anionic potentials also in the case of silicates depending upon the type of the linkage of SiO_4 tetrahedra and introducing the term of the ψ/SiO_4 potentials *(Grasselly,* 1958, 1959b), the possibility of comparing the stability relations of the different silicate anions on the basis of the variable ψ/SiO_4 potentials is given.

2. CONNECTION BETWEEN THE ψ/SiO_4 POTENTIALS AND SOME CONSIDERATIONS RELATING TO THE STABILITY RELATIONS OF THE DIFFERENT SILICATE ANIONS BASED ON THERMOCHEMICAL DATA.

Dealing with the distribution of different cations in the various silicates, *Ramberg* (1952) explains that by increase of the degree of the linkage, that is by the increase of the number of shared oxygen atoms, „. . . the nonbridging oxygen atoms which surround Fe, Mg, Ca etc., in olivine and pyroxene have a greater percentage of double-bond character

toward silicon in metasilicates than in orthosilicates." On this basis he assumes that the electronegativity value of oxygen increases stepwise from the nesosilicates toward the tectosilicates and due to this fact in the corresponding compounds the bonds between oxygen of the silicate anion and the neighbouring cation become more ionic in the given series. In an other paper studying the relative stabilities of the silicates, *Ramberg* (1954) establishes that the stability of the silicates is closely related to the degree of polarization of the oxygen, the more polarized it is the more stable are the silicates. According to *Ramberg* 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 is formed. Therefore, the stability of the silicate anions increases throughout the series: nesosilicates — inosilicates — phyllosilicates — tectosilicates. *Ramberg* in his paper referred to gives the heats of formation of simple potassium silicates from oxides to demonstrate by the increasing numerical value of ΔH the increase of the stability of the potassium silicates from the nesosilicates to the tectosilicates as shown in Table 1.

Table 1.

Silicate anion	ψ/SiO_4 average	Additive bonding energy adjusted to 24 O's of the silicate anions according to Keller in kg. cal.	The heats of formation from oxides of corresponding K-silicates according to Ramberg $-\Delta H_{298}$ kg. cal./2 g-equ.	The average Si—O distances determined in the single groups of silicates Å
SiO_4^{4-}	1,40	18 852	$43,8 \pm 3$	1,67
$Si_2O_7^{6-}$	1,22	21 511	—	1,65
SiO_3^{2-}	1,05	25 048	$64,5 \pm 7$	1,61
$Si_4O_{11}^{6-}$	0,96	27 290	—	
$Si_2O_5^{2-}$	0,87	29 981	$74,5 \pm 7$	1,60
SiO_2^{0}	0,70	37 320	$81,0 \pm 7$	1,58

The energy of formation of silicates may be computed by adding the energy constants according to *Huggins* and *Sun* (1946). These energy values are only approximate average values and are not suitable to compare quantitatively directly the different minerals on this basis. Therefore, as it has been stated by *Keller* (1954), „. . . the energies of formation of different minerals may be compared quantitatively if they are put on a uniform reference basis; this has been done by multiplying the molal energy for each mineral by a factor which adjusts the number of oxygen atoms in each mineral formula to a uniform mineral cell containing 24 oxygen atoms." Computing for the common silicate minerals the bonding energies adjusted to 24 O's, *Keller* established that a pronounced increase in bonding energy occurs in the sequence from the nesosilicates to the tectosilicates.

Huggins and *Sun* (1946) have computed the $\varepsilon_{Si^{4+}}$ for the different structures and *Keller* computed from these values the bonding energies

adjusted to 24 oxygen atoms for the different silicate anions, multiplying these values according to *Huggins* and *Sun* by the corresponding factors to be found in *Keller*'s paper referred to. The adjusted bonding energies according to *Keller* given in kg.cal. are also denoted in Table 1. The increase of the numerical values of these energies indicates the increase of the stability of the silicate anions.

Similarly are denoted in Table 1 the ψ/SiO_4 potentials characteristic of each silicate structure type as well as the average value of Si—O distances in the different groups given on the basis of the data taken from the referring literature *(Grasselly,* 1959b).

As it can be seen, the increase of the stability of the silicate anions from the nesosilicates toward the tectosilicates, indicated by the increasing numerical value of both the adjusted bonding energies according to *Keller* and the heats of formation of simple potassium silicates according to *Ramberg,* may be characterized by the ψ/SiO_4 potentials showing a decreasing tendency from the nesosilicates to the tectosilicates. The connection between the ψ/SiO_4 potentials and the adjusted bonding energies according to *Keller* is shown in Fig. 1.
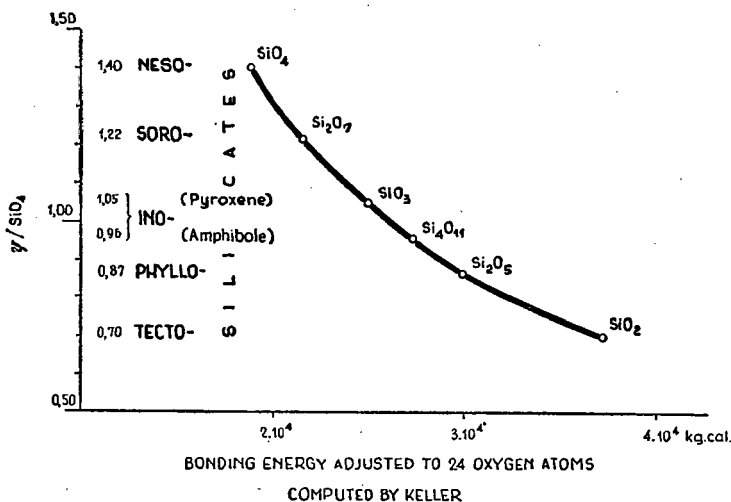
Fig. 1. The ψ/SiO_4 potentials in function of the adjusted bonding energies computed for the silicate anions by Keller

In the series of the potassium silicates the cation remains the same in each compound and only the structure type, only the silicate anion changes. Thus, it is presumable that the change of the heat of formation in the series is essentially resulted by the stability differences between the single silicate anion types, all the more, since within the silicates, the bond which contributes most to the bonding energy, is the high–energy Si-O bonds as it has been stated also by *Keller.* Thus, if in a series of simple silicates only the silicate anion changes and the cation remains

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the same, the increasing stability of the compounds can be characterized also by the decreasing ψ/SiO_4 potentials.

On the other hand, if in a series of silicates the silicate anion remains the same and the cations are changed. it is obvious that in the stability of the compounds the bonds cation-oxygen may play the role of a modifier, hence, the stability of the compounds can not be characterized by the anionic potential as it remains unchanged throughout the series. In Table 2 are denoted the heats of formation from component oxides given in kg.cal./mol. according to *Ramberg* as well as the additive bonding energies given in kg.cal./mol. computed from energy constant values of *Huggins* and *Sun,* the compound potentials introduced by *Szádeczky-Kardoss* (1954) and the ionic potentials.

Compound	Ionic potential of M2+	Compound potential of M2SiO4	Additive bonding energy	$-\Delta H_{298}$
			kg. cal./mol.	
Be₂SiO₄	5,88	4,38	5424	12,0 + 5
Mg₂SiO₄	2,56	2,17	4966	15,1 + 1
Ca₂SiO₄	1,89	1,72	4820	32,8 + 0,5
Ba₂SiO₄	1,40	1,40	4078	46,0 + 7

In such cases the increase of the stability of the compounds indicated exactly by increasing numerical value of heats of formation (measured in terms of heats of formation from oxides per two equivalent metal oxides) may be characterized by the decreasing compound potentials.

It has been mentioned above *Ramberg's* assumption that on increasing polymerization the bonds between silicon and nonbridging oxygen atoms have a greater percentage of double bond character. From the average Si—O distances given in Table 1 for each type the fact may be really established that the Si—O distances in average, from the nesosilicates toward the SiO_2 varieties, on the whole show a decreasing tendency (except the alumino-silicates as it can be stated from the data of the author's referred paper; *Grasselly,* 1959b) which seems to correspond to the increasing double-bond character of the Si—O bonds in the same direction as assumed by *Ramberg.*

The representation of the heats of formation in function of the ψ/SiO_4 potentials in the case of simple potassium silicates shows that the connection between the two values is nearly linear, that is the variable complex anionic potentials, the ψ/SiO_4 potentials characteristic of the single structure types of silicates are suitable to characterize the stability relations of the silicate anions, moreover in the series of simple silicates if the cation remains the same and only the type of the silicate anion changes, they are suitable to characterize the stability relations of the compounds too and not only that of the silicate anions, as it can be seen in Fig. 2.

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The similar connection may be established on representing the bonding energies adjusted to 24 oxygen atoms computed for the potassium silicates in function of the ψ/SiO_4 potentials as shown in Fig. 3.
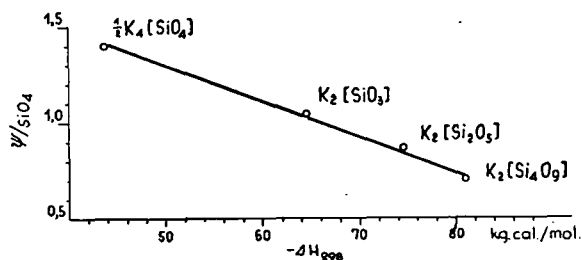

Fig. 2. Connection between the ψ/SiO_4 potentials and the heats of formation in the series of simple potassium silicates
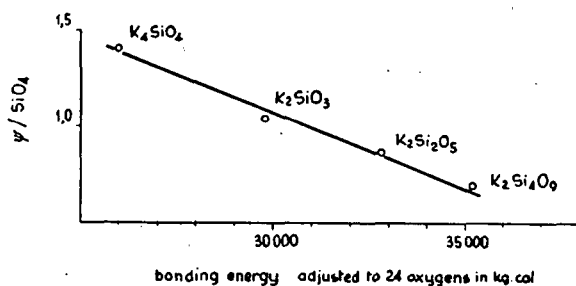

Fig. 3. Connection between the ψ/SiO_4 potentials and the adjusted bonding energies computed for the potassium silicates
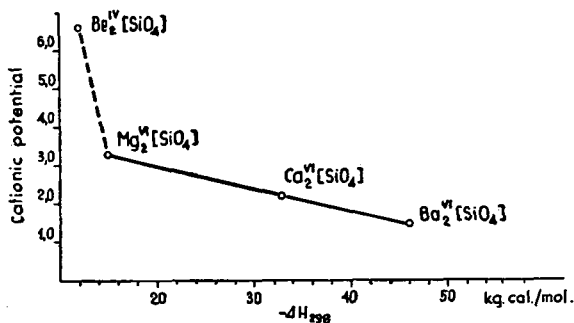

Fig. 4. Connection between the heat of formation and the cationic potentials in the series of alkaline-earth metal orthosilicates

Taking into consideration the alkaline-earth metal orthosilicates, the connection between their heats of formation and the cationic potentials seems also to be linear in the case of Mg_2SiO_4 — Ca_2SiO_4 — Ba_2SiO_4

and the stability increases by the decreasing cationic potentials (the same connection would be obtained taking the compound potentials instead of the cationic potentials). The point corresponding to the Be_2SiO_4 falls not along the line determined by the points corresponding to the three orthosilicate mentioned above. This can presumably be explained by the facts that partly the Be^{2+} in Be_2SiO_4 is 4-coordinated, whereas the Mg^{2+}, Ca^{2+} and Ba^{2+} ions are 6-coordinated in these orthosilicates, partly the Be^{2+} has a considerably higher polarizing force than the other three cations. This connection can be seen in Fig. 4.

To confirm that the decreasing complex anionic potentials — the ψ/SiO_4 potentials — and the decreasing compound potentials in general are suitable to characterize, to indicate the increase of the stability of silicate anions and silicate compounds, respectively, these values were compared with the adjusted bonding energies (Keller) and the heats of formation of the corresponding silicate anions and silicate compounds, respectively, taking into consideration the stability relations, partly in the series of the simple potassium silicates, partly in the series of the alkaline-earth metal orthosilicates. As it could be established, the increase of the stability is indicated by the increase of these values. The same is expressed by the decrease of the complex anionic potentials and the compound potentials, respectively.
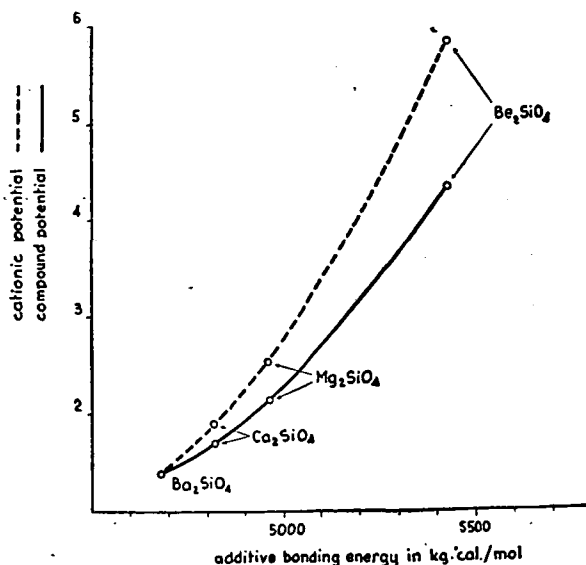
Fig. 5. Connection between the additive bonding energies and the cationic and compound potentials in the series of alkaline-earth metal orthosilicates

In the relation of the heat of formation and the additive bonding energy applied to express the increase of the stability, however, some contradiction seems to be revealed. In Table 1 the adjusted bonding

energies computed by *Keller* for the different silicate anions from the nesosilicates toward the SiO_2 increase as expected. Recalculating the additive bonding energies of the simple K-silicates to „mineral cells" containing 24 oxygen atoms as proposed by *Keller*, that is, computing the adjusted bonding energies of the simple K-silicates, the following increasing values will be obtained corresponding to the increasing heats of formation included in Table 1:

Compound	Bonding energy adjused to 24 O's
K_4SiO_4	26 028 kg.cal.
K_2SiO_3	29 832
$K_2Si_2O_5$	32 851
$K_2Si_4O_9$	35 202

In contrast, in the series of the alkaline-earth metal orthosilicates while the decrease of the cationic potentials and the compound potentials, respectively is in agreement with the increase of the heats of formation, on the basis of the additive bonding energies (obtained by simple adding the energy constants corresponding to the mineral formula; for example, the molal energy of formation of Ca_2SiO_4 is to compute as follows:

$$2 \times 839 \text{ kg.cal. } \varepsilon_{Ca^{2+}} \qquad\qquad 1{,}678$$
$$1 \times 3142 \text{ kg.cal. } \varepsilon_{Si^{4+}} \text{ in } SiO_4 \qquad 3{,}142$$
$$\text{Bonding energy, 1 mol } Ca_2SiO_4 \qquad 4{,}280 \text{ kg.cal.)}$$

the very opposite stability series would be given as it can be seen in Table 2. The same would result if these additive bonding energies would be recalculated to „mineral cells" containing 24 oxygen atoms. Hence, in the series of the alkaline-earth metal orthosilicates the stability relations on the basis of the heats of formation and the additive bonding energies, respectively, could be interpreted oppositely.

Of the two values the heat of formation can be considered as the more precise and real measure of the stability, since also *Huggins* and *Sun* have emphasized that the energy constants (ε_M values) are only approximate average values and „. . . that theoretically they *should not* and experimentally they *do not* give accurate energies of formation by simple additivity."

Dealing with the energy relationships of minerals in the *Bowen* reaction series on the basis of the adjusted bonding energies, the question has been arisen also by *Keller* „Is something wrong with the energy values . . . ?" The difficulties revealing in the interpretation of the *Bowen's* reaction series on the basis of adjusted bonding energies are the consequence of the fact that a so manifold process as the magmatic crystallization can not be interpreted and deduced by means of one factor — though be it the most precise — as it has been pointed out by *Keller*.

The contradiction afore-said supports the statement of *Huggins* and *Sun* cited above.

The agreement between the heats of formation and the adjusted bonding energies in the case of the K-silicates and the contradiction

revealing in the series of alkaline-earth metal orthosilicates between the two values mentioned may possibly be interpreted as follows.

Of the M-O-Si bonds within the silicates the strongest are in general the Si-O bonds, therefore, in the series of simple K-silicates, the silicate anion contributes most energy to the additive bonding energy and — being the cation, i. e., the K, the same in all compounds — the role of the cation to some extent may be neglected, all the more, since the bond K-O is considerably weaker than the Si-O bonds, and so the stability relations of the different silicate anions will characterize the stability relations of each K-silicate. The $\varepsilon_{Si^{4+}}$ values — the energy constants — are precisely determined values in the different silicate anions and since, partly the additive bonding energies of the different K-silicates are deduced from energy constant values characteristic of the given structures and partly the cation remains the same, the change of the bonding energies corresponds to the change of the heats of formation and the increase of these two values equally mean the increase of the relative stability of the successive members of the K-silicate series.

In contrast, in the series of alkaline-earth metal orthosilicates the silicate anion remains the same and the cation changes. The discrepancy may arise that the energy constants characteristic of the Be^{2+}, Mg^{2+}, Ca^{2+}, and Ba^{2+} ions are computed not from the molal heats of formation of silicates but from that of other compounds. Thus, the energy constants of the cations mentioned are determined from the molal heats of formation of their following compounds: Be^{2+}: BeO, $Be(OH)_2$, $BeSO_4$; Ca^{2+}: CaO; Mg^{2+}: MgO, $Mg(OH)_2$, $MgCO_3$, $MgSO_4$, $Mg_3(PO_4)_2$; Ba^{2+}: BaO, $Ba(OH)_2$, $BaCO_3$, $BaSO_4$, $Ba_3(PO_4)_2$, $BaWO_4$.

(*Huggins* and *Sun* (1946) have pointed out that the attraction between the cations and the surrounding oxygens contributes most to the ionic energy of formation of a solid compound and this attractive energy although changes from compound to compound, however, not too considerably, especially if the coordination number remains the same. The authors mentioned concluded that energy of formation (E_i) may be additively computed from the energy contributions originated from the attraction between the positive components and their neighbours. Thus,

$$E_i = \sum_M m_M \varepsilon_M,$$

where m_M is the relative number of the metal atoms, ε_M are constants characteristic of the element M deduced from experimentally determined E_i values. For details see the original paper referred to.)

Further is to be noted that the Be in Be_2SiO_4 is 4-coordinated, whereas the Mg, Ca and Ba in the corresponding silicates are 6-coordinated. It is probable that if the energy constants of the given cations were deduced from silicates, the change of the additive bonding energies and the change of the heats of formation also in the series of the alkaline-earth metal orthosilicates would correspond.

SUMMARY

To compare the stability relations of silicate anions of different types, the ψ/SiO_4 potentials depending upon the structure type, on the degree of polymerization of SiO_4 tetrahedra have proved to be suitable. The decrease of the ψ/SiO_4 potential values from the nesosilicates toward the tectosilicates indicates the increase of the stability of the corresponding silicate anions in the given direction.

If the stability relations of simple silicates of different structure types had to be compared, the ψ/SiO_4 potentials are suitable to serve as the basis for comparison in the case if only the silicate anion changes from compound to compound but the cation remains the same in all compounds.

If not independent silicate anions but different silicate compounds are in question, their stability relations can be characterized by the compound potentials introduced by *Szádeczky-Kardoss*, to be deduced from the cationic and the complex anionic potentials. The decrease of the compound potentials within a given series of silicates means the increase of the relative stability.

The statements, based on the ψ/SiO_4 anionic potentials, relating to the change of the stability relations of the silicate anions from the nesosilicates toward the tectosilicates are in agreement with that of based on both the heats of formation and the additive bonding energies.

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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.

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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.

<div align="center">

Table 1.

</div>

Structure type		Silicate anion	Average ψ/SiO_4
Nesosilicates		SiO_4^{4-}	1,40
Sorosilicates		$Si_2O_7^{6-}$	1,22
Cyclosilicates		$Si_3O_9^{6-}$ $Si_6O_{18}^{12-}$	1,05
Inosilicates	single chain	SiO_3^{2-}	1,05
	double chain	$Si_4O_{11}^{6-}$	0.96
Phyllosilicates		$Si_2O_5^{2-}$	0,87
Tectosilicates		$Al_2Si_2O_8^{2-}$	0,80
		$AlSi_3O_8^{1-}$	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 $Al_2Si_2O_8^{2-}$ anion, characteristic of anorthite, is 0,80, whereas that of the $AlSi_3O_8^{1-}$, 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

SiO₄ ← **Olivine** (2,12)
  1,40

  ↓

    SiO₃²⁻ **Hypersthene** (1,60)
    1,05

      ↓

      Diopside-augite
      (1,54—1,63)

        ↓

        Si₄O₁₁⁶⁻ **Amphibole** (1,51)   **Anorthite** (1,52) Al₂Si₂O₈²⁻
        0,96   0,80

          ↓   ↓

          Si₄O₁₀⁴⁻ **Biotite** (1,47)   **Albite** (1,41) AlSi₃O₈¹⁻
          0,87   0,74

            |_____   _____|
                   ↓   ↓
            SiO₂⁰ **Quartz** (1,38) ← **Potash feldspar** (1,38)
            0,70
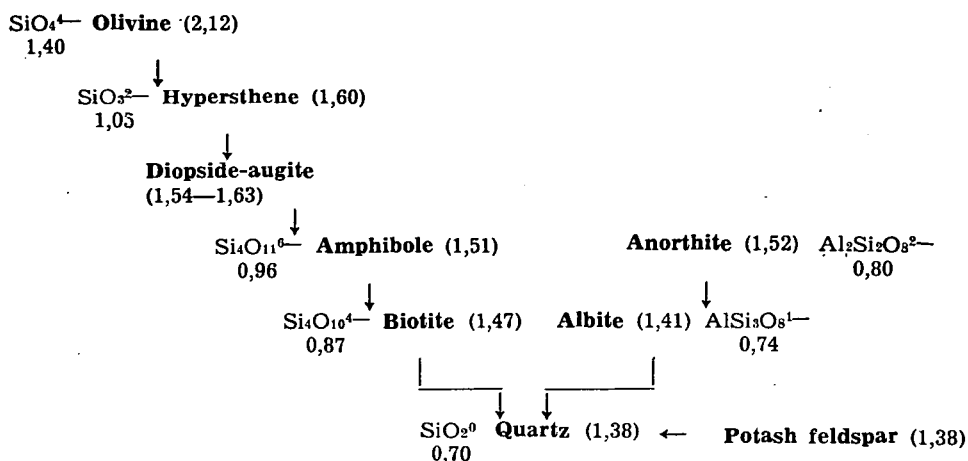
Fig. 1. The Bowen's reaction series of silicates with the corresponding
compound potentials and ψ/SiO_4 potentials

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 AlO₄ tetrahedra crystallize and the separation of silicates containing also AlO₄ 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:	
Nesosilicates-phyllosilicates		*Tectosilicates*	
Olivine $(Fe,Mg)_2SiO_4$	2,13	Anorthite $CaAl_2Si_2O_8$	1,52
Hypersthene $FeMgSi_2O_6$	1,60	Albite $NaAlSi_3O_8$	1;41
Diopside $CaMgSi_2O_6$	1,54	Orthoclase $KAlSi_3O_8$	1,38
Amphibole $(Mg,Fe,Ca)_7Si_8O_{22}(OH)_2$	1,51	Quartz SiO_2	1,38
Biotite $K(Mg,Fe,Al)_3Si_4O_{10}(OH)_2$	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 appearence 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* serties 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 availibility 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 $(Si + Al) : O$ 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 $Si_2O_5^{2-}$ 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 alkalies, 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 alkalies 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 $Si_2O_7{}^{6-}$ anion characteristic of the sorosilicates is 1,22 or that of the $Si_6O_{18}{}^{12-}$ 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 alkalies 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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THE ROLE AND SIGNIFICANCE OF THE COMPLEX ANIONIC POTENTIALS IN THE GEOCHEMISTRY

Part V. The periodicity of the complex anionic potentials

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1. INTRODUCTION

Szádeczky-Kardoss (1955) in his book „Geochemistry" dealing briefly with the connection between the ionic potentials of the complex-forming cations and their complex oxyanions states that the complex anionic potentials decrease as the corresponding cationic potentials increase within the same period whereas in the same groups of the periodic table both the complex anionic potentials and the cationic potentials decrease by increasing the number of the periods.

Grasselly has also dealt with (1959a) the connection between the ionic potentials and the corresponding anionic potentials attempting to characterize the stability relations of tetrahedral oxyanions on the basis of their complex anionic potentials.

On the basis of results of the studies of recent years relating to the complex-anionic potentials introduced in the geochemistry by *Szádeczky-Kardoss* (1954), it seems to be expedient to examine in detail how the complex anionic potentials change in the periodic system, and further what conclusions may be drawn from the periodicity of the complex anionic potentials.

2. THE CHANGE OF THE COMPLEX ANIONIC POTENTIAL IN THE PERIODIC TABLE

Denoting in the Periodic Table the ionic potentials of the complex-forming cations, the corresponding complex anionic potentials, the electrostatic energies of the complexes computed from ionic model as well as — if data were available — the energy constants according to *Huggins* and *Sun* (1946), it can be clearly observed that in the single periods the ionic potentials on the whole increase from left to right and correspondingly decrease the complex anionic potentials, whereas

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vertically, in the single groups of the Periodic Table both the ionic potentials and the complex anionic potentials decrease downwards. Exception can only be established in the relation of the series of Zr^{4+} — Nb^{5+} — Mo^{6+} and Hf^{4+} — Ta^{5+} — W^{6+} owing to the lanthanide contraction. Both the cationic potential of the Hf an Ta and the complex anionic potentials of their corresponding tetrahedral complexes are higher than they would be expected taking into consideration the generally downward revealing decreasing tendency of both values. In the case of Mo^{6+} and W^{6+} the corresponding values are the same, that is the ionic potential of both the Mo^{6+} and the W^{6+} is 10,34 and the complex anionic potential of the MoO_4^{2-} and the WO_4^{2-} anions, respectively, is 0,59.

Within the single periods neither the increase of the cationic potentials from left to right nor the decrease of the corresponding complex anionic potentials in the same direction are continuous during the whole period. For example, in the period 4, in the series of Ti—V—Cr—Mn placed before the iron-group, the ionic potential continuously increases and correspondingly decreases the complex anionic potential. The same can be stated in the series of Ga — Ge — As — Se placed in the same period but after the iron-group. However, between the two series, although both belong to the same period, the change of the cationic potentials and the complex anionic potentials, respectively, is not continuous.

Using the short-period form of the Periodic System the evidence of the change of the cationic potentials and the complex anionic potentials, respectively, is interferred especially vertically because in the single groups the elements of the subgroups are included and the most closely related elements are not always successively followed.

The change of the potentials is more clearly visible in the form of the periodic table used by *Fersman* wherein beneath the elements of the series Al — Si — P — S — Cl really the most closely related elements of the series Ga — Ge — As — Se — Br are placed and in the right side of that table beneath the elements of the series Ti — V — Cr — Mn directly follow the most closely related elements of the series Zr — Nb — Mo as in this form of the periodic table the elements of the subgroups — included in the short-period form by the single groups — are separated.

To demonstrate clearly the change of the values mentioned is especially advantageous the form of the Periodic Table according to *Szabó* and *Lakatos* (1954) including also the peculiarities of the *Fersman*'s table.

In this system the elements of the *Mendeleev*'s periods do not get into the same horizontal rows as the periodicity is associated with the periodicity of the shell structure and each row represents the completion of the single shells (except the alkalies and the alkali earth metals) as it is stated by these authors. In this system the subgroups are separated from one an other as in the *Fersman*'s table. The separation of the subgroups, the clear demonstration of the horizontally and vertically relationships among the elements by this system offer the possibility of

Fig. 1. Ionic potentials and energy constants of complex-forming cations as well as the complex anionic potentials and electrostatic energies of the corresponding tetrahedral oxyanions in the periodic table according to *Szabó* and *Lakatos*

a more distinct study of the change of ionic potentials and the complex anionic potentials as well as that of the energy constants and the electrostatic energies in the periodic table.

3. CONNECTION BETWEEN THE ELECTROSTATIC ENERGIES AND THE ANIONIC POTENTIALS OF THE TETRAHEDRAL COMPLEX OXYANIONS

Dealing with the stability relations of the complex oxyanions to characterize these stability relations the author *(Grasselly,* 1959a) has used the electrostatic energies computed from simple ionic model and expressed in arbitrary units. The anionic potentials and the electrostatic energies of the different complex anions are included in Table 1.

Table 1.

Complex anion	ψ_{MO_4}	U_{MO_4}	Complex anion	ψ_{MO_4}	U_{MO_4}
MgO_4^{6-}	1,75	0,63	VO_4^{3-}	0,89	12,96
BeO_4^{6-}	1,91	0,73	AsO_4^{3-}	0,92	13,81
GaO_4^{5-}	1,47	4,68	PO_4^{3-}	0,95	14,61
AlO_4^{5-}	1,52	4,93	MoO_4^{2-}	0,59	16,80
ZrO_4^{4-}	1,12	8,07	WO_4^{2-}	0,59	16,80
HfO_4^{4-}	1,13	8,11	TeO_4^{2-}	0,60	17,24
SnO_4^{4-}	1,15	8,34	CrO_4^{2-}	0,60	17,60
TiO_4^{4-}	1,16	8,47	SeO_4^{2-}	0,62	18,59
GeO_4^{4-}	1,21	9,09	SO_4^{2-}	0,64	19,80
SiO_4^{4-}	1,25	9,65	ReO_4^{1-}	0,30	21,50
NbO_4^{3-}	0,86	12,33	JO_4^{1-}	0,30	22,07
TaO_4^{3-}	0,87	12,39	MnO_4^{1-}	0,30	22,55
SbO_4^{3-}	0,88	12,76	ClO_4^{1-}	0,32	25,00

The connection between these values is illustrated in Fig. 2. The connections clearly shown in Fig. 2 as well as the conclusions to be drawn, emphasize the geochemical importance of the complex anionic potentials and the possibility of their manifold applications for interpretation of various geochemical problems.

From Fig. 2 the following may be concluded:

a) The connection between the complex anionic potentials and the electrostatic energies characterizing the stability relations of the tetrahedral oxyanions is linear.

b) The stabilities of the complex anions arranged along the lines from left to right downwards increase by decreasing complex anionic potentials.

c) The successive series beneath each other of the cations of complexes found on the lines going downward from left to right represent the single
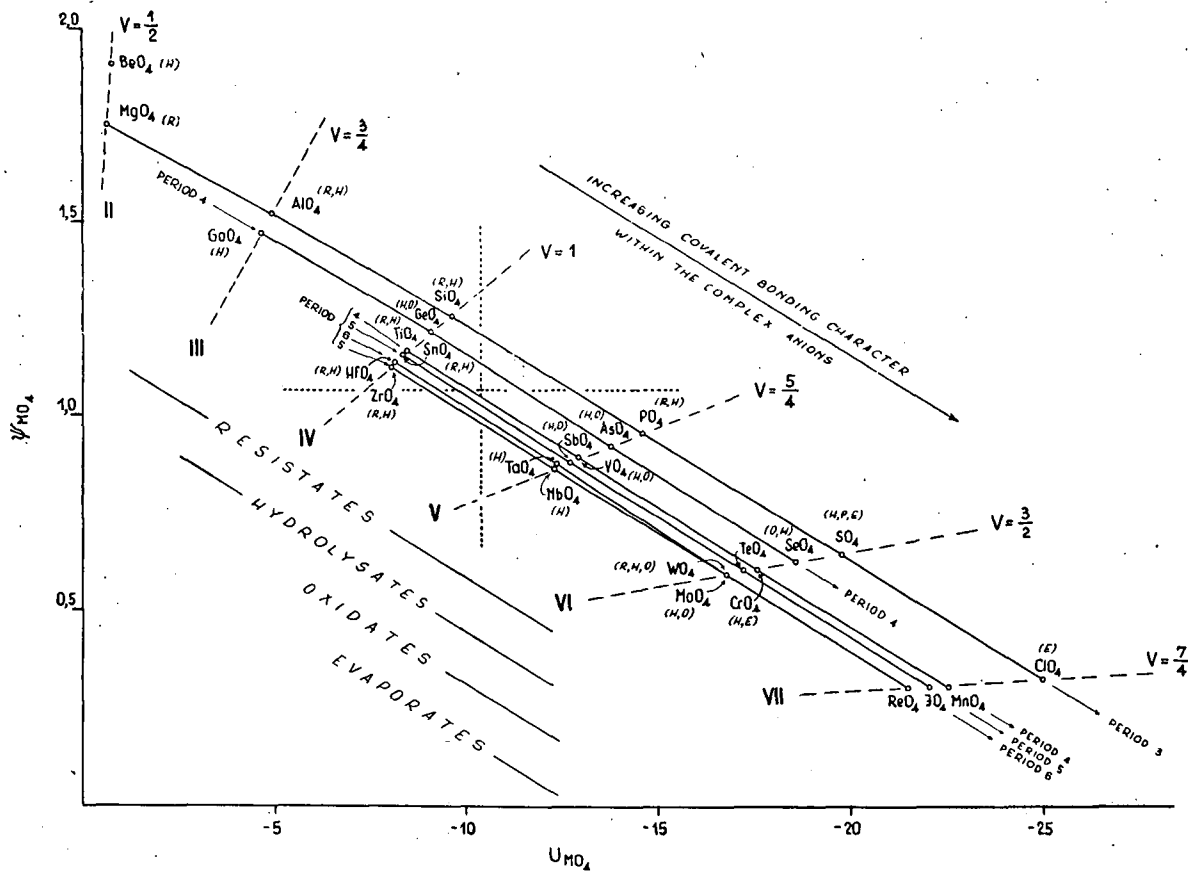
Fig. 2. The complex anionic potentials in the function of the
electrostatic energies

periods and the halves of the periods, respectively. The uppermost line would represent (apart from Be as from the period 2 it is only alone taken into consideration, however, calculating the anionic potential and the electrostatic energy, respectively, of the BO_4^{5-} too, the point denoting the place of this anion in Fig. 2 would be placed as expected) the period 3, whereas the two lines beneath it would correspond to the two halves of the period 4, under the elements of the period 3 follow directly the closely related elements of the period 4 that is the Ga, Ge, As, Se and on the third line the other elements of the period 4 are arranged, that is the Ti, V, Cr, Mn and their corresponding complexes, respectively. The following line represents the one half of the period 5 and again such elements succed firstly which are more closely related to the Ge, As, Se, that is the Sn, Sb, Te. Theoretically the elements of the other half of the period 5 would follow but owing to the lanthanide contraction the next line, determined by Hf, Ta, W and Re, represents the period 6 and on the last line representing the other half of the period 5 are placed the Zr, Nb and Mo and their corresponding complexes, recpectively. The lines representing the two periods at the W and Mo, respectively, coincide, since the charges of the two ions are equal and their radii are also identical due to the lanthanide contraction. Thus the Fig. reflects also the effect of the lanthanide contraction.

d) In the Fig. 2 the single groups of the periodic table similarly can be well distinguished. The stabilities of the complexes within each group increase by increasing complex anionic potentials from left to right upwards. This increase in the given direction is generally joined with the decrease of the number of periods (except the exchange of the period 6 and the one half of the period 5 mentioned above). This Fig. proves evidently that the complex anionic potentials are suitable to characterize the stability relations of complexes of elements belonging to different periods or groups of the periodic table as it has been pointed out by the author (*Grasselly*, 1959a).

e) Considering the chemical and crystallochemical peculiarities of the complexes enumerated, approximately two groups of the complexes may be distinguished in the Fig. The boundary between the two groups would be drawn about at $\psi_{MO_4} = 1,00$ and $U_{MO_4} = 10—12$ values, respectively. The complex anions of lower anionic potential than 1 and of higher electrostatic energy than 10 in general are stable and in aqueous solution too, are present as complexes and are not dissociated to ingredient ions and generally are the characteristic components of anisodesmic structures with considerably strong covalent bonding character as for example the ClO_4^{1-}, SO_4^{2-}, CrO_4^{2-}, AsO_4^{3-}, PO_4^{3-}, WO_4^{2-}, MoO_4^{2-} ions. On the other hand, the complex anions with anionic potential higher than 1 and with electrostatic energy lower than 10 are no longer so stable, in silicate melts, however, can be present as independent tetrahedral complexes. Some of these complexes exist also in crystals as real tetrahedral oxyanions, e. g., the SiO_4^{4-}, AlO_4^{5-}, GeO_4^{4-} as components of mesodesmic structures.

The differences in the bonding character and consequently in the peculiarities of the anions belonging to the two different groups are

shown also by the fact that in crystals, e. g., the SO_4^{2-}, WO_4^{2-}, SiO_4^{4-}, anions can be equally considered as real complex anions in physical sense, however, in aqueous solution at least the SO_4^{2-} and WO_4^{2-} ions occur, whereas the SiO_4^{4-} anion do not, although in silicate melts such anions also exist.

It is to note further that supposing only conditionally the existence of LiO_4, NaO_4 ,,complex anions" and computing their ,,anionic potentials", as well as electrostatic energies, the points determined by this values would get in the Fig. on the left side of the ψ axis which indicates that such complex anions can not exist and if such tetrahedra should occur in some crystals, they are complexes merely in geometrical sense but can not be considered as real complex anions in physical sense.

Matossi and *Krüger* (1936) have investigated among others the infrared reflection spectra of the Li_2WO_4 and the Be_2SiO_4. The two compounds from crystallographical viewpoint are isomorphous, the WO_4 groups corresponds to the SiO_4 groups and the LiO_4 tetrahedra existing in the structure of the Li_2WO_4 are formally analogous with the BeO_4 tetrahedra of the latter compound. In the infrared spectra, however, only the active vibration of short wave length of the WO_4 groups was to be detected, whereas that of expected for the LiO_4 tetrahedron was missing.

Consequently the authors mentioned have stated as follows: ,,Es ist zu bedenken, dass die SiO_4- Tetraeder einen ganz anderen Bindungs-mechanizmus bezüglich leichter Ionen aufweisen als die WO_4- Gruppe, was ja schon die Tatsache zeigt, dass in Lösungen zwar WO_4 aber nicht, SiO_4 Ionen vorkommen können. Das würde also heissen, dass zwar BeO_4- Tetraeder (Phenacit) und BO_4- Tetraeder (Danburit) als mit den SiO_4- Gruppen gleichberechtigte physikalische Baugruppen in den Silikaten existieren, nicht aber LiO_4- Tetraeder im Wolframat denen hier nur geometrische Bedeutung zukäme." These statements are shown in the Fig. too. The importance of distinguishing in crystals between complex anions in physical sense and complex groups merely in geo-metrical sense has been treated by the author in Part I of his paper concerning the role and significance of the complex anionic potentials in the geochemistry (*Grasselly*, 1959b).

f) The distribution of the complex anions in Fig. 2 in function of the anionic potentials and the electrostatic energies in some relations may be connected with the geochemical classification of the sediments too.

Goldschmidt on the basis of the cationic potentials divided the cations in three groups. Elements with lower ionic potential than 3, such the alkalies and alkaline-earth metals, are soluble and therefore they remain in solution during the weathering and the following transportation; elements of ionic potential between 3 and 12 are the characteristic elements of the hydrolysates and finally the elements with still higher ionic potentials form soluble complex oxyanions, e. g., S^{6+}, P^{5+}, C^{4+}, B^{4+}, N^{5+}.

Szádeczky-Kardoss (1955) in his book ,,Geochemistry" has pointed out that, though it was noted by *Goldschmidt* that the complex anions of the third groups mentioned above are characteristic partly of the resistates and partly of the evaporates — that is partly as components

of the minerals mostly resistant to the weathering and partly as components of sedimentary rocks, of minerals which are more soluble — however, this contradictory behaviour of the complexes of elements belonging to the same group, on the basis of the ionic potentials, was not yet satisfactorily interpreted.

Szádeczky-Kardoss pointed out that this interpretation may be given on the basis of the complex anionic potentials, since the minerals containing complex anions with highest anionic potentials, are most resistant to the weathering and therefore they become the minerals and complex anions, resp., characteristic of the resistates, whereas the greater part of complex anions — as the ionic potential during the complex-formation considerably diminishes compared with the corresponding cationic potentials — in the sediments will be separated with soluble cations of lower ionic potentials, forming the groups of evaporates and reduzates.

Further he dealt with the geochemical classification of the sediments on the basis of the compound potentials. In the following in connection with the problem of the geochemical classification of the sediments merely on the basis of the complex anionic potentials, without intending to go into a detailed discussion, the aim is to complete *Szádeczky-Kardoss*'s opinion with some contributions shown in Fig. 2.

Starting from the statement of *Rankama* and *Sahama* (1952) that the geochemical classification of sediments is not categorical, since the sedimentation processes are continuous and therefore the sediments of different types are usually mixtures of sediments belonging to two or three groups, it can be expected that neither on the basis of the cationic potentials nor on that of the complex anionic potentials is possible such an arrangement, such a sharp delimitation of the groups of elements and their corresponding complex anions, respectively, which would be characteristic only of the one or of the other group of the sediments.

For example PO_4^{2-} may occurs not only in the resistates (apatite, monacite, xenotime) but also in the hydrolysates (reprecipitated calcium-phosphate) and in phosphate sediments too. The AsO_4^{3-}, SbO_4^{3-}, VO_4^{3-} complex anions may be found in oxidate and hydrolysate sediments, similarly the Ga occurs partly in hydrolysates and partly in oxidates, Sn is secondarily enriched partly in resitates, (cassiterite), partly in Al-rich hydrolysates. The greater part of the sulphur is deposited in the hydrolysates and a considerably smaller part in the precipitates, but the sulphur occurs in the evaporates too, as gypsum and anhydrite as well as potassium-magnesium sulphates. The boron belongs partly to the resistates (tourmaline) but it occurs also in the hydrolysates, oxidates and evaporates too. Zirconium remains largely in the resistates, however, the hydrolysates also contain it.

Nevertheless, some general features may be established from the connection seen in Fig. 2.

It has been mentioned in this paper that the complex anions, included in Fig. 2, can be approximately divided into two groups. Also it is known that the division of the structures to anisodesmic, mesodesmic and isodesmic groups takes place on the basis of the *Pauling*'s electrostatic

valence. The electrostatic valence (V) is the charge (z) of the central cation divided by its coordination number (n):

$$V = \frac{z}{n}.$$

The structures, wherein bonds with electrostatic valence $V > 1$ (that is greater than the half of the charge of the anion) can be distinguished, are anisodesmic structures with discrete complex anions. The bonding within these anions are therefore stronger than the bonding between the complex anion and the neighbouring cations. In the former bonding a significant covalent character is revealed, whereas the latter is rather ionic. Characteristic anions are: NO_3^{1-}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, ClO_4^{1-} etc.

The structures with bonds the electrostatic valence of which is but the half of the charge of the oxygen, i. e., $V = 1$, are mesodesmic structures and the characteristic anions are firstly the SiO_4^{4-}, GeO_4^{4-}, BO_3^{3-} that is the characteristic anions of silicates, germanates and borates.

Finally, if in the given structure every bonding is weaker than the half of the charge of the oxygen, that is if $V < 1$, in such isodesmic structure discrete groups of ions in general can not be distinguished.

We have no intention to go into a detailed discussion of *Wickman's* investigations which are summarized in the work of *Rankama* and *Sahama* (1952), but we are only to refer to the following. According to *Wickman's* results the distribution of elements between sea water and the hydrolysates depends upon the crystal structure of their hydroxides. From the point of view of our present task the following are of importance cited according to *Rankama* and *Sahama* (1952): „If the electrostatic valence from the polarizing cation to the hydroxyl group is less than $\frac{1}{2}$, the charge of the oxygen will not show any tetrahedral splitting. Ionic bond is formed, and the hydroxide is readily soluble. If the electrostatic valence is $\frac{1}{2}$, one of the negative half-charges of oxygen will be occupied; and if the electrostatic valence is 1, two halves of the negative charge are required to bind the hydroxyl group to the cation. In these cases there remain unattached negative charges, which form hydroxyl bonds with the positive charges. If the electrostatic valence greater is than 1, a hydrogen bond is formed which is weak enough to cause the formation of a soluble complex anion."

Consequently taking into consideration the crystal structure of the hydroxides of elements, according to *Wickmann* ionic bonds are formed if $V < \frac{1}{2}$, hydroxyl bonds are formed if $\frac{1}{2} \leqq V \leqq 1$ and finally hydrogen bonds are formed if $V > 1$.

The change of the electrostatic valence, from which the conclusions mentioned above may be drawn, may be also observed in Fig. 2.

In Fig. are denoted that the single cations and their complexes, respectively, of what sediments are characteristic (R = resistates; $H =$

= hydrolysates; O = oxidates; P = precipitates; E = evaporates). It is to be seen that the single types actually can not be separated from each other. Nevertheless, the two groups distinguishable from crystallochemical viewpoint still show some regularity also from the point of view of the geochemical classification. Namely, the distribution of the elements and their corresponding complexes, respectively, in the function of the complex anionic potentials and the electrostatic energies, supports *Szádeczky-Kardoss*'s assumption that the complexes with higher anionic potential are characteristic rather of the resistates, whereas the complex anions with lower anionic potentials are characteristic rather of the evaporates and partly of the oxidates and precipitates. As it can be seen, among the complex anions deposited in the hydrolysates equally occur complex anions of both higher and lower anionic potentials. It is known that the resistates and hydrolysates are transported as particles of varying size suspended in solution, also in solid state, whereas the oxidates, precipitates and evaporates are deposited from material transported in ionic or colloidal solution to the site of deposition. The minerals of the evaporates, oxidates and precipitates are mostly of anisodesmic structure and the complex anions characteristic of these structures are the most stable ones and the bonding with expressed covalent character within these anions are stronger than the bonding between the complex anion and the surrounding cations. Thus, this bond can be relatively readily broken up and the compound dissolved and dissociated to cation and complex anion can be transported in ionic solution and under altered physicochemical conditions can be redeposited. On the contrary, the complex anions characteristic of the resistates (or hydrolysates) are less stable related to the groups of complex anions above-mentioned, and they are partly characteristic of mesodesmic structures. In the structure of such minerals within the complex anion, and between the complex anion and neighbouring cations, in the strength of these bondings, there are no such considerable differences (being the electrostatic valence of the bond within the complex anion equal even with the half of the charge of the oxygen, i. e., $V = 1$) as in the case of the anisodesmic structures, especially taking into consideration the main component of the resistates, that is the quartz, in the lattice of which the bonds are approximately of the same character and strength. Therefore, on weathering, these bonds do not break up so readily and the compounds, the minerals characteristic of the resistates or hydrolysates will be rather only mechanically disintegrated and in solid state transported and deposited as resitates or hydrolysates.

SUMMARY

To demonstrate the change of the complex anionic potentials and other values characteristic of ions in the periodic table, that of *Szabó* and *Lakatos* was used, because the separation of the subgroups, the clear demonstration of relationships both horizontally and vertically among the elements by this system, offer the possibility of a more distinct study of the change of ionic potentials and the complex anionic potentials as

well as that of the energy constants and the electrostatic energies in the periodic system.

On representing the values of anionic potentials of the different tetrahedral oxyanions in function of the electrostatic energies, computed on the basis of simple ionic model, the complex anions are arranged corresponding to the place of their central cation in the periodic system, that is on representing the correlation between the two values mentioned, essentially the periodic system is obtained, as it can be seen in Fig. 2. The arrangement of the complex anions gives clear informations partly from the stability relations of the tetrahedral oxyanions as well as the simple possibility of comparing the relative stabilities of the complexes is offered. Further, information is furnished concerning the peculiarities and behaviour of these anions also from chemical and crystallochemical viewpoint, inasmuch as two groups of the complexes may be distinguished. The complex anions with lower anionic potential than 1 in general are stable and are present also in aqueous solution as complex anions and are not dissociated into ingredient ions and are mostly characteristic of anisodesmic structures, on the other hand, the complex anions with higher complex anionic potential than 1 are no longer so stable, in silicate melt, however, they can be present as independent tetrahedral complexes.

The change of the *Pauling*'s electrostatic valence of the bonds within the complex anions may also be seen in Fig. 2.

The distribution of the complex anions represented in Fig. 2 in some relations may be connected with the geochemical classification of the sediments too. Though, neither on the basis of the cationic potentials nor on that of the complex anionic potentials is possible such an arrangement, such a sharp delimination of groups of elements and their corresponding tetrahedral oxyanions respectively, which groups would include elements characteristic only either of the one or of the other group of sediments, nevertheless, some general features may be established from the connection seen in Fig. 2.

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MONTMORILLONIT AUS DEN SPALTEN DES BASALTES VOM BADACSONY-BERG

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Ungarische Geologische Anstalt.

In den Spalten und Hohlräumen des Basaltes im Steinbruch bei „Steintor" am Badacsony-Berg (Komitat Zala in Ungarn) kommt hier und da eingelblichweißes, anscheinend gelartiges, betastend an Seife erinnerndes Material mit muscheligem Bruch und hornartigem Glanz vor. Dieses Mineral erwies sich auf Grund einer optischen, chemischen, DTA- und röntgenographischen Untersuchung als Montmorillonit.

Der Montmorillonit von Badacsony schrumpft ähnlich einem trocknenden Ton, wird rissig an der Oberfläche, dann zerfällt in Körner. Die Untersuchungen wurden mit solchem lufttrockenen Material gefertigt, welches monatelang an freier Luft gelegen ist.

Es ist bekannt, daß Montmorillonite, die in den Hohlräumen der Eruptive, so auch der Basalte, vorkommen, teils hydrothermalen Ursprungs, teils sekundäre Verwitterungsprodukte sind. Hierher sind die von Heide [1] aus Phonolith, von *Noll* [2], *Jung* [3] und *Schüller* [4] aus Basalten von Deutschland beschriebenen Vorkommen zu reihen. Vorkommen solcher Art wurden aus Ungarn bis jetzt noch nicht beschrieben.

Die hydrothermalen Bildungsbedingungen des Montmorillonits hat *Noll* [5] mit seinen synthetischen Untersuchungen aufgeklärt. Nach seinen Feststellungen entsteht Montmorillonit aus alkalihaltigen, schwach alkalischen Lösungen unter 400° C. Bei sehr hohem Alkaligehalt bilden sich Zeolithe, während bei einem niedrigeren, als zur Bildung der Zeolithe erforderlich, aber bei höherem Alkaligehalt, als zur Bildung des Montmorillonits nötig ist, entsteht Serizit (Hydromuskovit, Illit). Gleichfalls hat *Noll* [2] die Bildung des Montmorillonits aus der Verwitterung des Basaltes vom Vogelberge, bekannt gemacht.

Die äußeren Eigenschaften dieses letzteren, durch Verwitterung entstandenen Montmorillonits stimmen mit denen des von uns bearbeiteten Montmorillonits vom Badacsony-Berg überein. Es ist von diesen Verwitterungsprodukten am meisten festzustellen, daß sie Verwitterungsprodukte des mit ihnen unmittelbar in Berührung stehenden Basaltes sind, manchmal wurden sie aber durch die kreisenden Gewässer entlang den Spalten weiter gefördert.

Mit dem Problem des Montmorillonits beschäftigten sich zahlreiche Abhandlungen, die hier als bekannt vorausgesetzt werden. Auch mit seiner Struktur beschäftigten sich manche Forscher. Anstatt der Besprechung der verschiedenen Anschauungen weisen wir nur auf einige zusammenfassenden Arbeiten hin [6, 7, 8]. Nach unserer heutigen Auffassung bestehen die Minerale der Montmorillonit-Gruppe aus Pyrophyllit-, Talk-, Glimmer- oder Hydroglimmer-Schichtpaketen, aber ihre Gitter sind keine regelmäßig aufgebauten 3-dimensionalen Raumgitter. Die Silikatschichten sind zwar in der·Richtung der c-Achse parallel zueinander angeordnet, aber sie besitzen keine, in der Ebene der a- und b-Achse regelmäßig periodische Orientierung, das heißt, sie sind „statistisch ungeordnet", und so können sich keine hkl Netzebenen (periodisch identische Punktlagen) schräg zur c-Achse ausbilden und darum verschwinden die (hkl) -Reflexe aus ihrem Röntgenbild [9, 10]. In ihrer Tetraederschicht sind Si-Ionen durch Al, Fe^{3+}, in der Oktaederschicht Al durch 2-wertigen Ionen ersetzlich.. Infolgedessen tritt ein negativer Ladungsüberschuss auf, der durch zwischen die Schichten gelagerten Kationen ausgeglichen wird. Sie können zwischen die lose übereinander gelagerten Schichtpakete Wasser, ja sogar andere Flüssigkeiten aufnehmen und so hängt die c-Periode in ihrem Gitter von der Mächtigkeit des zwischengelagerten Wassers ab. Sie sind also „expandierte Pyrophyllite, Talke, Glimmer, oder Hydroglimmer". In ihrem Röntgenbild treten demnach nur die (001) — und (hk0) — Reflexe auf. Berücksichtigt man, daß die Mächtigkeit eines Pyrophyllit Schichtpaketes 6,6 Å beträgt, kommt eine Wasserschicht dazu mit 3 Å Mächtigkeit, so wird es verständlich, daß im Falle des zwischen den Silikatschichten gelagerten 5 H_2O, die c_0 Gitterkonstante ungefähr 21 Å beträgt, während bei Zwischenlagerung eines H_2O-s, die Gitterkonstante in der c-Richtung 9,6 Å ist. Das zwischen den Schichten gelagerte Wasser kann reversibel beseitigt werden.

Montmorillonit enthält aber nicht nur Zwischenschicht-, und Adsorptionswasser, sondern auch Koordinationswasser, auf dessen Besprechung wir später zurückkehren werden.

Die Struktur des Illits ist ähnlich, wie die des Montmorillonits, aber einige der Si-Positionen sind durch Al ausgefüllt. Die Zusammenfassung der dies bezüglichen Anschauungen findet man bei *Grim* [11]. Der zufolge der Si → Al Substitution auftretende Überschußladung wird durch die zwischen den Silikatschichtpaketen gelagerten K^+-Ionen ausgeglichen. Gelingt es also das K^+ von den Schichtpaketen ohne Zerstörung der Struktur beseitigen, so kann man aus Illit Montmorillonit erhalten. *White* [12] hat experimental erwiesen, daß die Illit → K^+ + Montmorillonit Umwandlung möglich ist, wenn man Illit mit Natriumkobaltinitrit oder $MgCl_2$ behandelt. Es ist auch die umgekehrte Umwandlung möglich (9).

Nach dieser kurzen Schrifttumsübersicht kehren wir zur Untersuchung des Tonminerals von Badacsony zurück. In Anbetracht dessen, daß hier die Aufklärung der Funktion des Wassers von größter Bedeutung ist, beschäftigen wir erstens mit der Differential Thermoanalyse des Minerals. Die DTA-Untersuchung hat *Vera Koblencz* verfertigt. Nach dem DTA-Diagramm (Fig. 1.) verliert das Mineral das Wasser in 4 Anteilen. Die 4 Endothermspitzen zeigen sich nahe bei 150°, 550°, 700° und

900°. Die größte ist die erste Endothermspitze. Die Wasserabgabe beginnt sich unter 100°, erreicht ihren Höhepunkt bei 150° und endet bei 300°. Die Spitze entspricht dem Adsorptions- und Zwischenschichtwasser des Montmorillonits. Die folgenden drei Spitzen zeigen die Abgabe des Koordinationswassers. Die bei 550° sich zeigende Spitze entspricht [13] Illit, die bei 700° auftretende des oktaedrisch gebundenen Koordinationswassers des Montmorillonits, während die bei 900° entwickelnde Endothermspitze zeigt, daß man hier wirklich mit einem tetraedrisch Koordiniertem Wasserüberschuß zu tun hat, von welchem wir in unseren vorigen Abhandlungen [14, 15] nachgewiesen haben, daß die HO-Gruppen an die Stelle jener Oxygene der Tetraederschicht treten, die mit der Oktaederschicht in Koordination stehen. Man muß hier auf jene interessante Tatsache hinzeigen, daß die bei 700° auftretende Endothermspitze des Montmorillonits der Endothermspitze des Hydromuskovits und Hydroparagonits entspricht (14). Wir erwähnten, daß Illit sich in Montmorillonit und Montmorillonit in Illit umwandeln kann [9, 12], während der Zusammenhang zwischen Illit und Hydromuskovit selbstverständlich ist. Sie unterscheiden sich nur in ihre Korngröße; ihre Röntgenbilder sind nahe identisch, sie sind voneinander nur mit DTA-Untersuchung, eventuell durch ihre Brechungsindizes unterscheidbar.
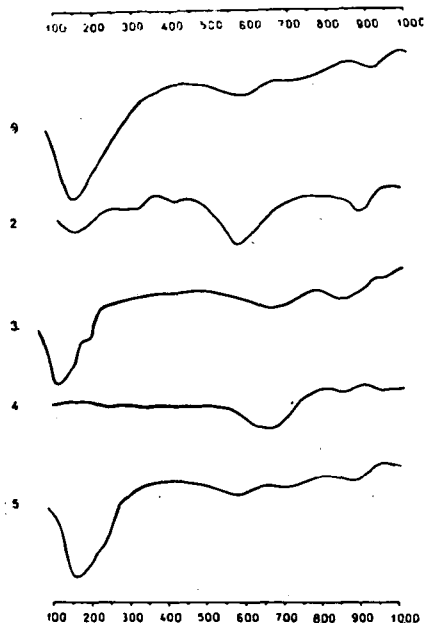
1. Montmorillonit, Badacsony, »Steintor«, Koblencz, V.
2. Illit, Alexander County, Illinois. Grim, Rowland (15).
3. Montmorillonit, Budatétény. Koblencz, V.
4. Hydromuskovit, Nagybörzsöny. Koblencz, V.
5. Montmorillonit + Illit, Pécs-Mecsek. Koblencz, V.

Fig. 1.

Montmorillonit unterscheidet sich von Illit und Hydromuskovit auf Grund der Bisherigen in erster Linie darin, daß die übereinander geschichteten Schichtpakete des Montmorillonits in der Ebene der a- und b-Achse nicht gleich genau orientiert sind. Infolgedessen wächst ihre Oberfläche außerordentlich an, andererseits ist ihre Aneinanderfügung lückenhaft zufolge der schwachen Verbindungskräften der desorientierten Schichpakete und nach unserer Ansicht kann die zufolge der Entstehung dieser Lücken auftretende Kapillarität in erster Linie der Hauptgrund der flüssigkeitaufnehmenden Fähigkeit des Montmorillonits sein.

Mit der Wasseraufnahme (Quellung) des Montmorillonits beschäftigten sich schon zahlreiche Abhandlungen. Mit diesen wünschen wir eine Diskussion nicht entspannen und vernachlässigen ihre Besprechung. Wir verweisen nur auf die schon erwähnten zusammenfassenden Arbeiten [6, 7, 8], und in den Weiteren teilen wir nur unsere eigene Beobachtungen und Berechnungen mit. *Maria Földvári-Vogl* war so verbindlich ihre Briefwechsel mit *R. C. Mackenzie* (Aberdeen) zur Ansicht zu überreichen. *Mackenzie* betrachtet den um 700°, bezw. um 550° Wasser abgebenden Montmorillonit für normalen, bezw. anomalen Montmorillonit, obwohl er selbst diese Bezeichnung nicht für zutreffend hält. Ähnliche Anschauungen erkennt auch *W. F. Cole* (23) als sein eigen an.

Die chemische Analyse des Tonminerals von Badacsony hat *Vera Tolnay* gefertigt. Der DTA-Untersuchung entsprechend führte sie die Wasserbestimmung innerhalb 5 Temperatur-Grenzen aus bis zu 100°, 300°, 600°, 700° und 1000°. Von den Analysen-Angaben ließen wir TiO_2, was nach unseren Kenntnisse von Rutil-Verunreinigung herrühren kann, sowie das Apatit-Verunreinigung bedeutende Spur P_2O_5 weg, gleichfalls ließen wir das Adsorptions- und das Zwischenschicht-Wasser bis zu 300° weg. Der Rest wurde in 100% umgerechnet. Das gebliebene Wasser wurde in HO-Gruppen umgerechnet, das zweierlei oktaedrische Wasser gesondert berechnet (bis 600° und 700°), gleichfalls wurde das tetraedrisch koordinierte Wasserüberschuß umgerechnet.

Der atomaren Zerlegung der Analyse hindurch berechneten wir die Ionenzahlen. Entsprechend der Strukturformel des Montmorillonits und Illits nahmen wir $O + OH = 12$, als Grundlage der Berechnung, da $O + OH$ in der Struktureinheit konstant ist, und insgesamt 12 Positionen ausfüllen kann. Zur auf dieser Weise erhaltenen Struktureinheit berechneten wir das zuerst außer Rechnung gelassene Adsorptionswasser und das Zwischenschichtwasser.

Der Gang und die Ergebnisse der Berechnung sind folgende:
Die Analyse:

```
SiO₂    ............................... 48,82 %
TiO₂    ...............................  0,31 „
Al₂O₃   ............................... 13,37 „
Fe₂O₃   ...............................  2,36 „
FeO     ...............................  0,84 „
MnO     ...............................  0,07 „
CaO     ...............................  1,84 „
MgO     ...............................  5,72  „
K₂O     ...............................  0,55 „
Na₂O    ...............................  0,11 „
Li₂O    ...............................  0,017 „
H₂O (bis   100°)    .............. 14,26 „
H₂O (bis   300°)    ..............  5,87 „
H₂O (bis   600°)    ..............  3,29 „
H₂O (bis   700°)    ..............  0,58 „
H₂O (bis 1000°)    ..............  1,40 „
CO₂     ...............................  0,00 „
P₂O₅    ...............................  0,04 „
                                        ──────
                                        99,447 „
```

Die Form der Analyse ist nach den erwähnten Abzüge und in 100%
umgerechnet:

```
SiO₂    ............................... 61,82 %
Al₂O₃   ............................... 16,93 „
Fe₂O₃   ...............................  2,99 „
FeO     ...............................  1,06 „
MnO     ...............................  0,09 „
CaO     ...............................  2,33 „
MgO     ...............................  7,24 „
K₂O     ...............................  0,70 „
Na₂O    ...............................  0,14 „
Li₂O    ...............................  0,03 „
H₂O     ...............................  6,67 „
                                        ───────
                                        100,00 „
```

Der Gang der Berechnung der Ionenzahlen (wir haben die Bestand-
teile in wachsender Reihe der Ionenradien geschrieben):

Atom %-e		Atomquotiente	Ionenzahlen	Ionenzahlen ($O + OH = 12$)
Si	28,90 %	1,02882	1028,82	3,823 ⎫ 4
Al	8,96 „	0,33211	332,11	0,177 ⎬
				1,057 ⎭
Fe^{3+}	2,09 „	0,03743	37,43	0,139 ⎫
Mg	4,37 „	0,17965	179,65	0,667 ⎪
Li	0,01 „	0,00085	0,85	0,003 ⎬
Fe^{2+}	0,83 „	0,01480	14,80	0,055 ⎪
Mn	0,07 „	0,00125	1,25	0,005 ⎭
Na	0,10 „	0,00450	4,50	0,017 ⎫
Ca	1,67 „	0,04155	41,55	0,154 ⎬
K	0,58 „	0,01479	14,79	0,055 ⎭
HO	12,60 „	0,74085	740,85 ⎫ 3229,62	2,753 ⎫ 12
O	39,82 „	2,48877	2488,77 ⎭	9,247 ⎭

Vor der Aufstellung der Strukturformel nehmen wir unter Besichti-
gung die Ionenzahlen. Von größter Wichtigkeit ist die Aufklärung der Rolle
des viererlei Wassers. Die um 550° auftretende von der 4 Endothermspitzen
entspricht Illit [13]. *Mackenzie* und *Cole* (siehe eher) nennt diese für ano-

male Montmorillonitspitze. Diese lassen wir einstweilen außer Acht. Die ausführliche Auswertung der übrigen 3 Spitzen findet man in der Abhandlung von *M. Földvári-Vogl* [16] mitsamt den betreffenden Schrifttumsangaben. Auf Grund dieser entstammt die erste Endothermspitze von dem Adsorptionswasser, von Zwischenschichtwasser und von dem Hydratwasser der umtauschbaren Kationen, und so ist sie nicht charakteristisch für das Tonmineral. Aus der Form der Spitze kann man nur auf das umtauschbare Kation folgern. Der Montmorillonit von Badacsony ist ein Ca-Montmorillonit, wie auch die Mehrzahl der ungarischen Montmorillonite. Die zweite Endothermspitze um 700° deutet die Entweichung des oktaedrisch gebundenen Wassers an. In Anbetracht der Auswertung der dritten, um 900° auftretenden Endothermspitze nimmt *M. Földvári-Vogl* keinen bestimmten Standpunkt auf Grund der bisherigen Kenntnisse ein, und sagt sie nur für eine Annahme, daß jene aus der Entweichung der tetraedrisch gebundenen Wassers herrühre. Die nach den 3 Endothermspitzen auftretende Exothermspitze hängt von Ersetzungen der Oktaederschicht ab [16, S. 54.]. Die $Al \rightarrow Fe^{3+}$ Substitution kann die Exothermspitze gänzlich verschwinden lassen. Hier ist eine $Al \rightarrow Fe^{3+}$ Substitution wirklich vorhanden, wie es aus der untenstehenden Strukturformel sichtbar ist, dementsprechend ist keine Exothermspitze an der DTA-Kurve wahrzunehmen. Zur Aufklärung der Rolle der vier Endothermspitzen führten wir, wie erwähnt wurde, die Wasserbestimmung bei 5 verschiedenen Temperaturen aus. Das unter 300° entweichende Wasser nahmen wir nicht in Betracht bei der Berechnung der Strukturformel, da dieses koordiniertem Wasser nicht zu betrachten ist. Die Berechnung ergab aus dem über 300° entweichenden Wasser eine Ionenzahl $(OH)_{2,753}$ anstatt $(OH)_2$, das heißt, einen HO-Überschuss $(OH)_{0,753}$ der auf Grund unserer bisherigen Untersuchungen [14, 15] tetraedrisch substituierten HO -Gruppen entspricht. Berechnet man gesondert das bis 600°, 700° und 1000° entweichende Wasser, erhält man folgende Ionenzahlen:

$$
\left.
\begin{array}{l}
\text{bis } \ \ 600° \ \ldots\ldots\ldots\ldots \ (OH)_{1\cdot719} \\
\text{„ } \ \ \ \ 700° \ \ldots\ldots\ldots\ldots \ (OH)_{0\cdot303} \\
\text{„ } \ 1000° \ \ldots\ldots\ldots\ldots \ (OH)_{0\cdot731}
\end{array}
\left.\begin{array}{c} \\ \\ \end{array}\right\} (OH)_{2\cdot022} \ \right\} (OH)_{2\cdot753}
$$

In unseren früheren Abhandlungen wurde nachgewiesen [14, 15], daß die negative Ladungsabnahme, die von dem tetraedrisch gebundenen HO-Überschuss verursacht wurde, im Falle des Hydromuskovits von Nagybörzsöny durch die Ladungsabnahme der einsubstituierten 2-wertigen Ionen der Oktaederschicht ausgeglichen wird, da die Zahl der 2-wertigen Ionen der Oktaederschicht (eventuell mitsamt den Äquivalenzzahlen der nicht ausgefüllten oktaedrischen Positionen) gleich genau mit der Ionenzahl des HO-Überschusses ist. Untersucht man dementsprechend den Montmorillonit von Badacsony, so steht sich heraus, daß die Zahl der in die Oktaederschicht tretenden 2- und 1- wertigen Ionen gleich 0,730 ist, das heißt, sie ist gleich mit der Zahl der tetraedrisch gebundenen HO-Ionen: 0,731, vorausgesetzt, daß man die Rolle des Ca-s einstweilen außer Acht läßt. Also auch hier sind jene strukturellen Regeln gültig [15, 24], die in Beziehung mit dem Hydroantigorit von Dunabogdány abgeleitet wurden.

Diese Regeln in Betracht genommen ist die Struktureinheit des Ton-minerals von Badacsony folgendermaßen aufzuschreiben:

$$(Al_{1,057} Fe^{3+}_{0,139} Ca_{0,101} | Mg_{0,667} Fe^{2+}_{0,055} Mn_{0,005} Li_{0,003})^{[6]} (Si_{3,823} Al_{0,177})^{[4]} \cdot O_{9,247} (OH)_{2,753}$$

$$(K_{0,055} Ca_{0,053} Na_{0,017})$$
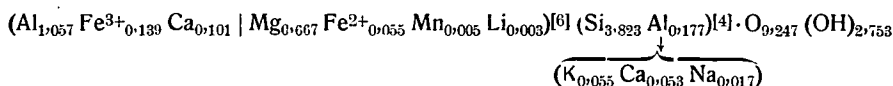
Aus der Struktureinheit berechnet: M = 369,81. Dies beträgt 78,97% der Analyse. Rechnet man aus dem 20,13% des unter 300° gemessenen Wassers das nicht koordinierte Wasser, enthält man als Ergebnis $5,2 H_2O$, aus welchem 3,7 mol H_2O Adsorptionswasser ist (bis 100°) während das größtenteils Zwischenschichtwasser innerhalb 100——300° entweicht.

Wir müssen noch jene Ladungsfragen aufklären, die mit der in die Oktaederschicht substituierten $Ca_{0,101}$ verknüpft sind. Wir sahen in den Vorigen, daß man durch direkte Messung die Zahl der oktaedrischen HO-Ionen 2,022 gefunden hat. Die Überzahl ist aller Wahrscheinlichkeit nach ein unbedeutender Fehler der Wasserbestimmung, oder ergibt sie sich eventuell daraus, daß das Zwischenschichtwasser von der Gewohnheit abweichend nicht innerhalb 100—400°, sondern nur bis 300° gemessen wurde. (Der Messungsfehler kann auch aus der geringen Menge des zur Bestimmung verbrauchten Materials herrühren.) Da das gesamte koordi-nierte Wasser $(OH)_{2,753}$ beträgt, ist der HO-Überschuß 0,753, infolgendes-sen sind noch 0,011 Ca zu den 2-wertigen oktaedrischen Kationen hinzu-fügen, um den Ladungsausgleich dadurch zu erreichen. Der Rest ist $Ca_{0,090}$. Wenn man nach einer bekannten Rechnungsweise $2/_3$ Teil dieses Calciums zur Substitution der oktaedrischen 3-wertigen Ionen anwendet, gleicht 0,030 Ca den zufolge der $Al^{3+} \rightarrow Ca^{2+}$ Ersetzung frei gewordenen Ladungsüberschuß aus, das nach älterer Auffassung in die Zwischen-schicht gelangt, bleibt es aber nach unserer Auffassung in der Oktaeder-schicht, dä die Äquivalenzzahl der Oktaederschicht nur samt diesem 5,247 ausmacht, das heißt, die Äquivalentenabnahme ist 0,753 dem 0,753 HO-Überschuß entsprechend. Die Ionenzahl der Oktaederschicht beträgt nun 2,027, was der Ionenzahl der Oktaederschicht eines dioktaedrischen Montmorillonits genau entspricht.

Auf Grund des Gesagten kann man die Struktureinheit folgender-maßen aufschreiben (das Adsorptionswasser vorläufig in Betracht nicht genommen):

$$(Al_{1,057}Fe^{3+}_{0,139}Ca_{0,060}|Ca_{0,011}Mg_{0,667}Fe^{2+}_{0,055}Mn_{0,005}Li_{0,003})^{[6]}.$$

$$Ca_{0,030}$$

$$\cdot (Si_{3,823}Al_{0,177})^{[4]}O_{9,247}(OH)_{2,753} \cdot \sim 1H_2O$$

$$(K_{0,055}Ca_{0,053}Na_{0,017}).$$
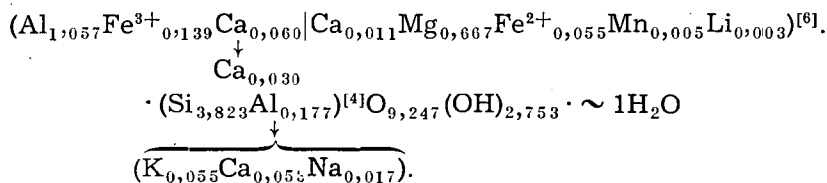
Die 2-wertigen Ionen, die den Ausgleich der negativen Ladungsab-nahme zustande bringen, welche durch den tetraedrisch gebundenen HO-Überschuß verursacht wurde, sind in der oktaederischen Koordination mit einer Senkrechte abgesondert. Den abgesonderten Teil in Betracht

nicht genommen ist es aus der Strukturformel ersichtlich, daß man hier mit einem Eisen-Calcium-Montmorillonit zu tun hat.

Auf Grund des Gesagten muß man feststellen, daß man bezüglich des Montmorillonits, so wie bezüglich der Hydroglimmern (Illite, Hydromuskovite) aufgestellte Strukturformeln größtenteils für verfehlt betrachten muß, und die Revision dieser Strukturformeln erforderlich ist, denn der tetraedrische HO-Überschuß wurde bei der Berechnung der Strukturformeln einerseits absolut außer Acht gelassen, oder andererseits wurde ihre Stellung nicht richtig gedeutet (z. B. bei *McConnel*, 17).

Die *Röntgenaufnahme* und die Ausmeßung der Linien des Pulverdiagramms des Tonminerals von Badacsony hat *Margarete Melles* im Laboratórium der Ungarischen Geologischen Anstalt gefertigt. Für ihr freundliches Zusammenwirken drücken wir auch bei dieser Gelegenheit unseren Dank aus. Die Aufnahme wurde mit CuK$\bar{\alpha}$-Strahlung und Ni-Filtration fertiggebracht (10mA, 38kV, 10^h).

Vergleicht man die gemessenen Linien mit jenen eines bekannten Illits von Illinois [18], dann stellt sich heraus, daß die Linien des Montmorillonits von Badacsony mit den stärksten und mit einigen mittelstarken Linien des Illits genau übereinstimmen. Die gemessenen Reflexionen des Montmorillonits von Badacsony teilen wir nebst den berechneten Angaben *Winkler*s [19] und mitsamt den entsprechenden Reflexionen eines Illits von Illinois [18] mit. (1. Tabelle).

Tabelle 1.

Gemessene Angaben		Montmorillonit [19] (berechnet)			Illit [18]		
d_{hkl}	I	d_{hkl}	I	Indizes	d_{hkl}	I	Indizes
10,03	4	9,5—20	st	001	9,98	st .	002
7,66	1 - 2 verschw.	6,4	schw	001	—	—	—
4,44	4	4,42	st	110	4,47	st	110
		4,47		020			
3,34	2	3,23	m	003	3,31	m	006, 024
2,55	4	2,54	st	200	2,56	st	20$\bar{2}$
		2,57		130			
1,681	3	1,69		300	1,65	schw	1,3, $\overline{10}$
		1,69	m	150			
		1,70		222	1,64	m	312
1,493	4	1,49		213	1,50	st	060
		1,49	st	060			
		1,50		024			
1,287	2	1,287	m	153	1,29	m	400
		1,285		260			
				(400)			

Aus der Tabelle ist ersichtlich, daß man hier mit zwei (001) Reflexionen zu tun hat. In Anbetracht dessen, daß wir hier mit einem lufttrockenen Material gearbeitet hatten, in welchem der Wassergehalt zwischen den Schichten keine bestimmte Mächtigkeit hat, müssen wir nach den Angaben der Analyse 1—1,5 Mol Zwischenschichtwasser annehmen und, wenn die Mächtigkeit eines Pyrophyllit-Schichtpaketes 6,6 Å beträgt, und die Mächtigkeit eines Mol Wasserschichtes 3 Å, insgesamt 9,6 Å ist, dann entspricht die 10,03 c_0-Periode unseres Montmorillonits einem solchen Montmorillonit, welcher ungefähr $1H_2O$ Zwischenschichtwasser enthält, während die schwache, verschwommene d = 7,66 Reflexion einem beinahe entwässertem Montmorillonit entspricht.

Wir erwähnten, daß die Übereinstimmung der Montmorillonit-Linien mit jenen des Illits aus der 1. Tabelle ins Auge fallend ist, aber diese Linien stimmen auch mit den stärksten und mittel starken Linien des Hydromuskovits von Nagybörzsöny [14] gut überein. An dem DTA-Diagram kann man außer der von reversibelem Wasser verursachten Endothermspitze die Spitzen des Illits [13, 16] und des Hydromuskovits [14, 15] wahrnehmen. (S. Fig. 1.) Wir müssen gleich darauf denken, daß dieser Montmorillonit nicht anderer ist, als ein Hydromuskovit-Illit, der aus in der ab-Ebene nicht orientierten Schichtpaketen besteht, und der den überwiegenden Teil seines Alkaligehaltes verloren hatte, welcher Vorgang nach White's [12] Feststellungen möglich ist. Auch seine Strukturformel kann man, als Fe-Ca-Illit aufschreiben. Nur die Röntgenanalyse und die Gitterkonstanten könnten entscheiden, daß man hier dennoch mit keinem Hydromuskovit-Illit, sondern mit einem Montmorillonit zu tun hat, welcher in seinem Gitter eventuell noch einen geringen unumgewandelten Illit enthält die Menge der Alkalien zu Grunde dieser Feststellung genommen. Das Mineral kann man für ein Gemisch eines Normal-Montmorillonits mit wenig Illit nicht betrachten, da in diesem Falle jene Endothermspitze in DTA-Diagramm vorherrschen müßte, die die Abgabe des Koordinationswassers des Montmorillonits (des Hydromuskovits) zeigt. Den Angaben dieses Montmorillonits stechen aber die strukturellen, Eigenschaften des urspünglichen Illits und Hydromuskovits ebenso hervor, wie auch die konstitutionellen Eigenschaften der Eltern an den Gegebenheiten des Kindes hervorstechen.

Die Gitterkonstanten aus den Reflexionen (400), (060), und (001) berechnet, sowie β-Winkel aus der (20$\bar{2}$) Reflexion für Illit gerechnet, erhalten wir die folgenden Angaben:

$a_0 = 5,17$, $b_0 = 8,96$, $c_0 = 10,07$, ($\beta = 95° \ 16,5'$)

Vergleichen wir diese Angaben mit den Hofmann—Endell—Wilm'schen Angaben (20) des Montmorillonits, sowie mit den entsprechenden Angaben des Hydromuskovits von Nagybörzsöny:

	a_0	b_0	c_0	β
Montmorillonit (Badacsony):	5,17	8,96	10,07	(95°16,5')
„ [20]:	5,17	8,94	15,2	~ 90°
Hydromuskovit (Nagybörzsöny [14]):	5,20	9,00	20,00	95° 3'

Die zweierlei Angaben von Montmorillonit unterscheiden sich nur in

der c_0-Periode, die natürlich von dem Zwischenschichtwasser abhängt. Wir können nicht in jener Meinung übereinstimmen, daß die c_0-Periode nur bei Entwässerung um 400° etwa 10Å sein könnte [9]. Das Röntgenbild des Montmorillonits von Badacsony wurde nämlich aus einem lufttrockenem Material verfertigt, dennoch ist c_0 gleich 10,03. Den β-Winkel pflegt man bei Montmorillonit $\sim$ 90° angeben, aber *Gruner* [21] vermeint, daß Montmorillonit monoklin wäre und indiziert er die innerste Reflexion gleich Illit mit (002). *Maegdefrau und Hofmann* weisen aber diese Auffassung ab [22]. Diese Meinung müssen wir wirklich ablehnen, da in diesem Falle für c_0 einen Wert um 20 erhielten, was 4—5 Mol Zwischenschichtwasser bedingte, während wir in unserem Material zwischen 100—300° nur ungefähr 1,5 Mol H_2O gemessen hatten. Wir haben hier also wirklich mit Montmorillonit zu tun, der aus solchen Hydromuskovit-Illit-Schichten besteht, die ihre Alkali-Gehalt verloren haben. Diese Schichtpakete stellen sich zufolge des Verlustes ihres Alkali-Gehaltes nicht orientiert übereinander, da das 12-er koordinierte K(Na) das die Schichtpakete zusammenklammerte, fehlt. Die d_{hkl} =1,64 Angabe der (312) Reflexion des Illits ist ziemlich von der d = 1,69 Linie des Montmorillonits entfernt. Die übrigen Illit-Linien entsprechen keiner (hkl) Netzebene. (S. die 1. Tabelle.)

Der mittlere Brechungsindex des Montmorillonits von Badacsony in einem Gemisch von Mandelől (n = 1,478) und Chlorbenzol (n = 1,522) gemessen wurde 1,49 gefunden. Dieser ist viel niedriger als jener des Illits und etwas kleiner als der des Montmorillonits im allgemeinen, aber stimmt mit dem Brechungsindex des von *Jung* und *Schüller* [3, 4] aus dem Basalt des Grossen Dolmars bei Meiningen beschriebenen Montmorillonits genau überein.

Es sind folgende aus den Untersuchungsangaben des Montmorillonits vom Badacsonyberg festzustellen:

1. Das Mineral ist auf Grund seiner speziellen Konstitutionsformel ein Ca-Montmorillonit, für welche jene strukturellen Regeln gültig sind, die in Beziehung mit den Hydroglimmern besprochen wurden [14, 15], das heißt: a) die Abnahme der Äquivalentzahlen der Oktaederschicht ist gleich mit der Zahl der tetraedrisch Koordinierten HO-Ionen. Diese Abnahme wird durch die Einführung in die Oktaederschicht jener 2- und 1-wertigen Ionen hervorgerufen, deren Zahl der Ladungsabnahme der Oktaederschicht entspricht, b) die Äquivalentzahl der Zwischenschichtkationen (K,Na,Ca) ist gleich mit der Zahl der Si $\rightarrow$ Al-Substitution, c) während gleichen die übrigen Ca-Ionen die Äquivalentzahl der Oktaederschicht in solcher Weise aus, das die Äquivalentzahl der oktaedrisch koordinierten Ionen jener strukturellen Regeln genau entspricht, die in unseren vorigen Mitteilungen besprochen wurden [14, 15].

2. Die Linien des Pulverdiagramms des Montmorillonits von Badacsony stimmen mit den stärksten, sowie mit einigen mittelstarken Linien (001 und hk0 Reflexe) des Hydromuskovits, bezw. Illits genau überein.

3. Von den 4 Endothermspitzen des DTA-Diagramms entspricht die erste (zwischen 100—300°) dem Adsorptions und Zwischenschichtwasser,

die bei 550° ist die charakteristische Endothermspitze des Illits und die bei 700° ist jene des Hydromuskovits, während die bei 900° sich zeigende Endothermkrümmung auf den tetraedrisch koordinierten HO-Überschuß verweist.

Auf Grund obigen Angaben ist der Montmorillonit von Badacsony nicht anderes, als ein Ca-führender, desorientierter Hydromuskovit-Illit, aus welchem die 12-er koordinierten Ionen (K,Na,Ca) größtenteils ausgelaugt wurden.

Unsere Ergebnisse gaben zugleich Antwort auf die Frage der bei DTA-Untersuchung auftretenden sogenannten „normalen", und „anomalen" Illit-, bzw. Montmorillonit-Spitzen.

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