

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

By. GY. GRASELLELY

Institute for Mineralogy and Petrography,
University of Szeged, Hungary

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 corre- sponding K-silicates according to Ramberg — ΔH_{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 ± 3	1,67
$\text{Si}_2\text{O}_7^{6-}$	1,22	21 511	—	1,65
SiO_3^{2-}	1,05	25 048	64,5 ± 7	1,61
$\text{Si}_4\text{O}_{11}^{6-}$	0,96	27 290	—	1,60
$\text{Si}_2\text{O}_5^{2-}$	0,87	29 981	74,5 ± 7	1,58
SiO_2^0	0,70	37 320	81,0 ± 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 $\epsilon_{\text{Si}^{4+}}$ 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.

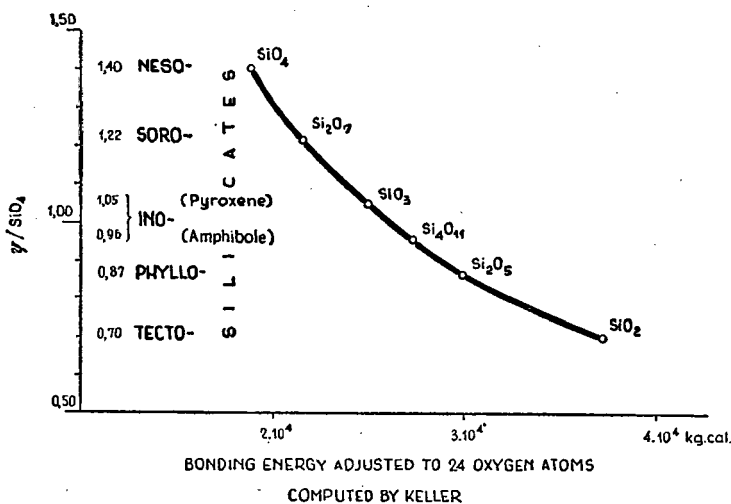


Fig. 1. The ψ/SiO_4 potentials in function of the adjusted bonding energies computed for the silicate anions by Keller

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

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 $M_2\text{SiO}_4$	Additive bonding energy kg. cal./mol.	$-\Delta H_{298}$
Be_2SiO_4	5,88	4,38	5424	$12,0 \pm 5$
Mg_2SiO_4	2,56	2,17	4966	$15,1 \pm 1$
Ca_2SiO_4	1,89	1,72	4820	$32,8 \pm 0,5$
Ba_2SiO_4	1,40	1,40	4578	$46,0 \pm 7$

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.

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.

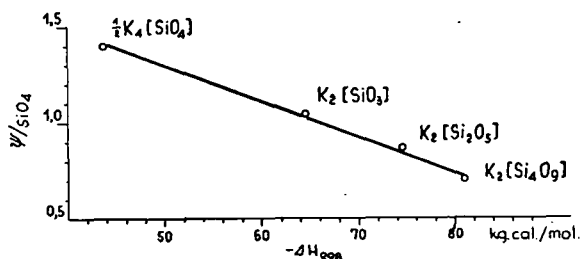


Fig. 2. Connection between the ψ/SiO_4 potentials and the heats of formation in the series of simple potassium silicates

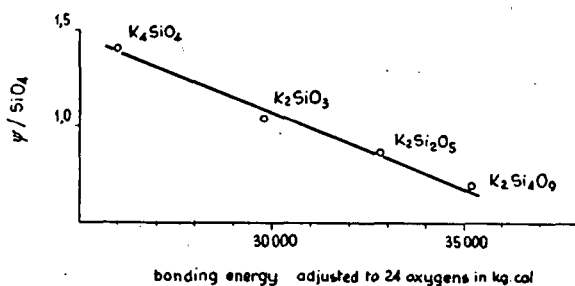


Fig. 3. Connection between the ψ/SiO_4 potentials and the adjusted bonding energies computed for the potassium silicates

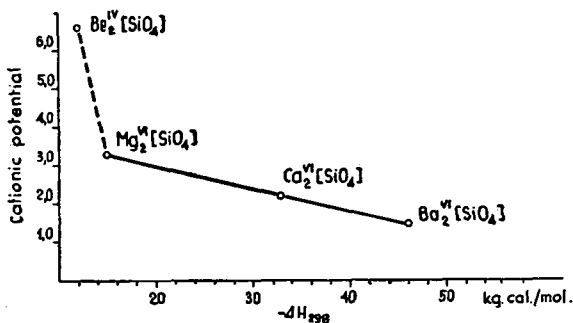


Fig. 4. Connection between the heat of formation and the cationic potentials in the series of alkaline-earth metal orthosilicates

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 $\text{Mg}_2\text{SiO}_4 - \text{Ca}_2\text{SiO}_4 - \text{Ba}_2\text{SiO}_4$

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 orthosilicates 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.

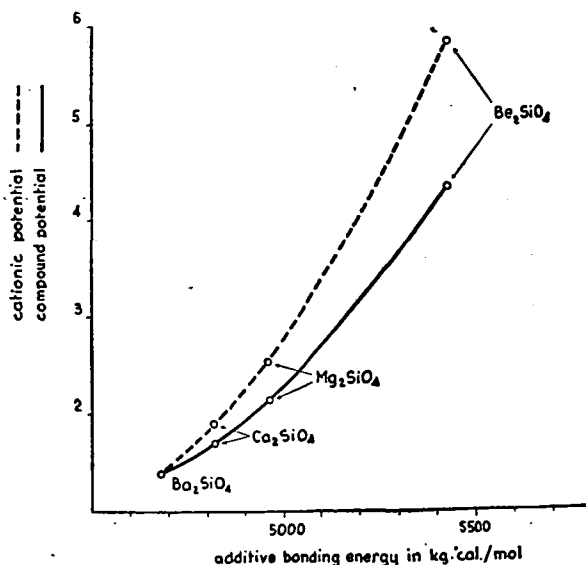


Fig. 5. Connection between the additive bonding energies and the cationic and compound potentials in the series of alkaline-earth metal orthosilicates

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
$\text{K}_2\text{Si}_2\text{O}_5$	32 851
$\text{K}_2\text{Si}_4\text{O}_9$	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:

$$\begin{array}{r}
 2 \times 839 \text{ kg.cal. } \epsilon_{\text{Ca}^{2+}} \qquad \qquad \qquad 1,678 \\
 1 \times 3142 \text{ kg.cal. } \epsilon_{\text{Si}^{4+}} \text{ in } \text{SiO}_4 \qquad \qquad \underline{3,142} \\
 \text{Bonding energy, 1 mol } \text{Ca}_2\text{SiO}_4 \qquad \qquad \underline{4,280 \text{ kg.cal.}}
 \end{array}$$

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 $\epsilon_{Si^{4+}}$ 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_1) may be additively computed from the energy contributions originated from the attraction between the positive components and their neighbours. Thus,

$$E_1 = \sum_M m_M \epsilon_M,$$

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_1 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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