RELATIVE STABILITIES OF SOME SIMPLE SILICATES AS RELATED TO THE POLARIZATION OF THE OXYGEN IONS

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ABSTRACT

The stabilities of simple silicates relative to the component oxides are discussed. Some general relationships between stability of these silicates and size and charge of the cations are pointed out. The larger the size of the noble gas type cation and/or the lower its charge, the more stable the silicate relative to the free oxides. This is explained in principle by a simple crystal model in which the oxygen ion becomes unsymmetrically polarized in the resultant field created by Si^{4+} and the metal ions. The model is put in a mathematical form, and it can be shown by the equation how the $Si^{4+}-O^{2-}$ bonds become strengthened and the cation-O^{2-}bonds weakened when the oxides react to form a silicate. The energy release combined with the strengthening of the $Si^{4+}-O^{2-}$ links is usually larger than the energy absorption connected with the weakening of the cation-O^{2-} links thus resulting in a net energy release when stable silicates form from the free oxides. This exothermic energy is related to the degree of polarization of the oxygen ion; the more polarized the oxygen the greater the energy release and the more stable the silicate relative to the free oxides.

The empirical relationship between degree of polymerization in silicates and the field strength of the cation is discussed.

Although many of the stability relationships can be accounted for in principle by employing the concept of polarization and contrapolarization of the oxygen ions, it is realized that the concept of resonance between ionic and covalent bindings also can explain the observations. The reason that the idea of polarization is made use of in this paper is that it can be put more readily in a mathematical form.

INTRODUCTION

It is a known crystal chemical fact that the stability of silicates and other oxysalts is related to the polarizing power of the cations or their tendencies to form covalent bonds with oxygen (Goldschmidt, (1927), Cartledge (1951), Ramberg (1952).

One may say that a cation with strong polarizing power or pronounced tendency to make covalent bonds loosens the bonds within the oxyanions, like SiO_4^{4-}, PO_4^{3-}, CO_3^{2-}, etc., thus causing a splitting up of the oxysalts into the free oxides. Cations with small polarizing power allow strong bonds to form within the oxyanion and do therefore make stable silicates or other oxysalts. This phenomenon is very significant for the understanding of formation of silicates and deserves more attention from mineralogists and geochemists than it has hitherto attracted. Not only is the question whether an element can form silicates or not controlled by

TABLE 1

Li $Li_2Si_2O_5$	Be Be_2SiO_4	B none	C none
Na $Na_2Si_2O_5$	Mg $MgSiO_3$	Al Al_2OSiO_4	Si none (quartz)
K $K_2Si_4O_9$	Ca $CaSiO_3$	Sc $Sc_2Si_2O_7$	Ti none
Rb $Rb_2Si_4O_9$	Sr $SrSiO_3$	Y $Y_2Si_2O_7$	Zr $ZrSiO_4$
Cs $Cs_2Si_4O_9$	Ba $BaSi_2O_5$	lanthanides ?	Hf $HfSiO_4$
X	Ra ?	Ac ?	Th $ThSiO_4$

TABLE 2

Ion	Ionic potential	Type of silicates				
		ortho	pyro	meta	phyllo	$Si_4O_9^{2-}$-type
C^{4+}	26	none	none	none	none	none
B^{3+}	15	none	none	none	none	none
Ti^{4+}	6.25	none	none	none	none	none
Be^{2+}	5.88	Be_2SiO_4	none	none	none	none
Al^{3+}	5.26	Al_2OSiO_4	none	none	none	none
Zr^{4+}	4.60	$ZrSiO_4$	none	none	none	none
Th^{4+}	3.64	$ThSiO_4$	none	none	none	none
Sc^{3+}	3.61	—	$Sc_2Si_2O_7$	none	none	none
Y^{3+}	2.83	—	$Y_2Si_2O_7$	none	none	none
Mg^{2+}	2.56	Mg_2SiO_4	—	$MgSiO_3$	none	none
Ca^{2+}	1.89	Ca_2SiO_4	—	$CaSiO_3$	none	none
Sr^{2+}	1.57	Sr_2SiO_4	—	$SrSiO_3$	none	none
Ba^{2+}	1.40	Ba_2SiO_4	—	$BaSiO_3$	$BaSi_2O_5$	none
Li^{+}	1.28	Li_4SiO_4	—	Li_2SiO_3	$Li_2Si_2O_5$	none
Na^{+}	1.02	Na_4SiO_4	—	Na_2SiO_3	$Na_2Si_2O_5$	none
K^{+}	0.75	K_4SiO_4	—	K_2SiO_3	$K_2Si_2O_5$	$K_2Si_4O_9$
Rb^{+}	0.67	Rb_4SiO_4	—	Rb_2SiO_3	$Rb_2Si_2O_5$	$Rb_2Si_4O_9$
Cs^{+}	0.61	Cs_4SiO_4	—	Cs_2SiO_3	$Cs_2Si_2O_5$	$Cs_2Si_4O_9$

the field strength around the cations, but so is the maximum degree of polymerization which silicates can have. This becomes apparent when the information compiled in Tables 1 and 2 is considered. In Table 1 some electropositive elements are arranged according to their position in the periodic table and underneath each element the most polymerized silicate known of this element is given. (Polymerization means in these cases sharing of O by two Si atoms. Throughout this paper only anhydrous silicates with but one kind of cation are considered.) The tendency to form silicates in general and polymerized silicates in particular increases from the upper right side of Table 1 toward its lower left side. The small highly charged ions like B^{3+} and C^{4+} (Ti^{4+}) do certainly not form simple anhydrous silicates at all, whereas the large and low-charged alkali ions form silicates with a maximum degree of polymerization.

The elements in the table make noble gas type cations. In this case therefore, the ionic potential, charge/radius, is an adequate relative measure of the field strengths.[1] The ionic potentials of the cations are given in table 2 together with some of the monocationic anhydrous silicates which the elements are known to form. There is a very obvious correlation between ionic potential and the maximum degree of polymerization found in the silicates.

TABLE 3. HEATS OF FORMATION OF M_4SiO_4 AND M_2SiO_4 FROM COMPONENT OXIDES, GIVEN IN Kcal/MOL.[1]

Silicate	$-\Delta H_{298}$	Silicate	$-\Delta H_{298}$
Li_4SiO_4	49.0 ± 5	Be_2SiO_4	12.0 ± 5
Na_4SiO_4	83.7 (?)	Mg_2SiO_4	15.1 ± 1
K_4SiO_4	87.5 ± 7	Ca_2SiO_4	32.8 ± 0.5
Rb_4SiO_4	—	Sr_2SiO_4	—
Cs_4SiO_4	—	Ba_2SiO_4	46.0 ± 7

[1] Data from Kubaschewski and Evans (1951).

RELATIVE STABILITIES OF ORTHOSILICATES

Let us discuss the stabilities of orthosilicates relative to the free metallic oxide and silica. The known heats of formation show that the stability, measured in terms of heats of formation from oxides per two equivalent metal oxides,[2] increases with decreasing ionic potential (Table 3).

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[1] If noble gas type ions are compared with non-noble gas type ions, the ionization potential would be a better indicator of relative field strengths than the ionic potential (See Ahrens (1953) and Ramberg (1953)).

[2] At low temperature the entropy term in the free-energy equation: $\Delta F = \Delta H - \Delta S T$ is small for silicates so that the difference between heats of formation ΔH, and free-energy of formation, ΔF, is negligible. ΔH is therefore a sufficient accurate stability indicator for our task.

This can now be explained qualitatively by means of a rather simple crystal-energetic model by considering the relative energies of the M—O and the Si—O bonds in the free oxides and in the orthosilicates respectively. (M^{z+} is the cation.) The Si—O bond is (usually) stronger in the orthosilicate ion than in quartz because the Si—O bond is more covalent, or O^{2-} is more polarized in SiO_4^{4-} than in quartz where oxygen is shared between strongly contrapolarizing Si^{4+} ions. On the other hand the M—O link is weaker in a silicate than in the metal oxide. The question whether or not an orthosilicate is stable relative to the free oxides depends then to a large extent upon the degree of strengthening of the Si—O bonds and weakening of the M—O bonds when metal oxides and quartz unite to form a silicate. The strengthening of the Si—O bond represents a decrease in energy thus tending to stabilize the silicate whereas the weakening of the M—O bond represents an increase in energy thus working against the formation of the silicate. The heat of formation of the silicate from the constituent oxides is then the difference between these two bond-energy changes.

When we now compare the energies of the Si—O and M—O bonds in the oxides and silicates respectively, we shall sacrifice some accuracy for the benefit of simplicity in order to make the basic principles clear. Thus, for example, repulsive energy between penetrating electron clouds will be disregarded. Furthermore the repulsive energy between oxygen ions and between the positive ions respectively, will be disregarded, hoping that this energy will be approximately equal in a silicate and in the corresponding free oxides. After these simplifications are made, the only energy difference to be expected between free oxides and equivalent amount of orthosilicate is that due to change of attractive energy of M—O and Si—O links in the oxides and the silicate respectively. Such an energy change is partly due to polarization of the oxygen ions, partly to covalent bonds. It is not easy to distinguish between polarization of O^{2-} and covalent sharing of electrons between oxygen and attached cation. Since the energy changes due to polarization can be calculated, at least in principle, whereas there is no easy way of calculating covalent bond energy in silicates, we shall treat the crystals from the viewpoint of varying degree of polarization of the oxygen ion. *It appears then that the stability of the silicates is closely related to the degree of polarization of* O^{2-}, *the more polarized it is the more stable are the silicates.*

In the simple metal oxides and in quartz each oxygen is more or less symmetrically surrounded by one kind of cation, the fields of which cancel out approximately in the center of the oxygen ion. One can therefore, as an approximation, consider the oxygen ions in the coordination lattices of the free oxides as not being polarized at all. The electrostatic energy of each Si^{4+}—O^{2-} link in quartz is therefore given by the simple equation:

$$E_q = -\frac{4e2e}{d_{\mathrm{Si-O}}}, \text{ where } d_{\mathrm{Si-O}} \text{ is the} \tag{1}$$

Si—O distance in quartz. The repulsive energy due to overlapping of the electron clouds is disregarded.

The electrostatic energy of each M^{z+}—O^{2-} bond in the metal oxide is:

$$E_{\mathrm{M-O}} = -\frac{ze2e}{d_{\mathrm{M-O}}}, \tag{2}$$

where $d_{\mathrm{M-O}}$ is the M—O distance, and any repulsive energy is disregarded. These electrostatic bond energies must now be compared with the energies of the corresponding bonds in the silicates where O^{2-} is polarized by the Si^{4+} ion. Each O^{2-} ion in the orthosilicates has one Si^{4+} and m M^{z+} attached to itself. In Be_2SiO_4, for example, there are two Be^{2+} bound to each oxygen (i.e., $m=2$); in forsterite (Mg_2SiO_4) there are three Mg^{2+} attached to each oxygen and the same is true for γ Ca_2SiO_4 and Ba_2SiO_4 and possibly also for Sr_2SiO_4 which all have the Al_2BeO_4 type of structure (Wyckoff, 1951, vol. 2).

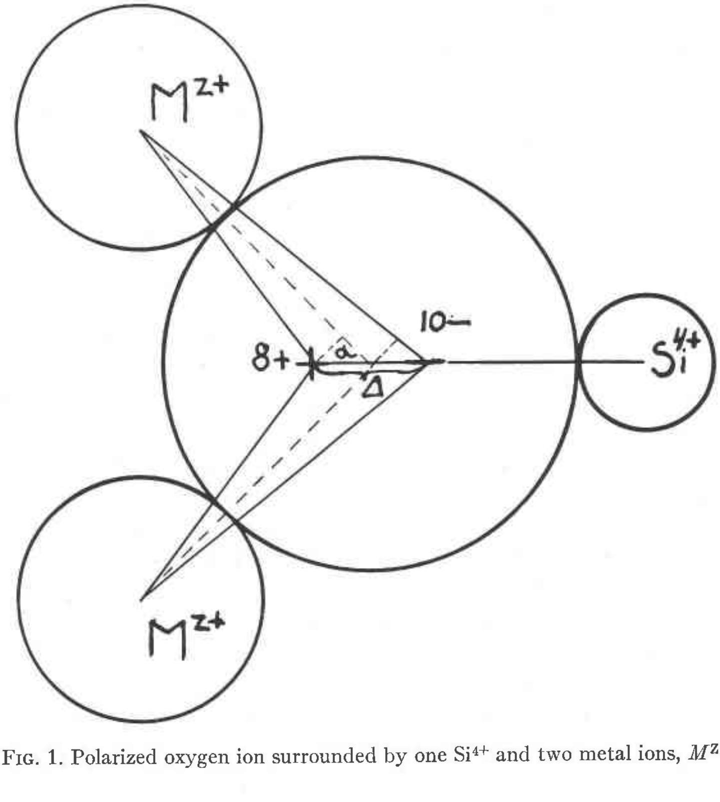

FIG. 1. Polarized oxygen ion surrounded by one Si^{4+} and two metal ions, M^{Z+}.

In order to demonstrate the effect of polarization of O^{2-} we shall assume that Si^{4+} and the m M^{z+} ions are arranged in a symmetric fashion around O^{2-} in such a way that the resultant field of the m M^{z+} ions is parallel to the line through Si^{4+} and the center of oxygen (Fig. 1). O^{2-} is then situated in a field with a strength equal to the difference between the field caused by Si^{4+} and the resultant field of the m M^{z+} ions. For stable silicates the field around Si^{4+} is the stronger so that O^{2-} is unsymmetrically polarized, i.e. a dipole moment is induced in O^{2-} which may be pictured as if the 10 electrons on O^{2-} are displaced a distance $1/2\Delta$ toward Si and the oxygen nucleus with its 8 positive charges is displaced $1/2\Delta$ away from Si, (Fig. 1). For simplicity, let the distance from the center of the polarized O^{2-} to Si and M respectively, be d_{Si-O} and d_{M-O} as in the free oxides. The energy of Si^{4+} with respect to the polarized oxygen then is:

$$E'_{Si-O} = -\frac{4e10e}{d_{Si-O} - \frac{1}{2}\Delta} + \frac{4e8e}{d_{Si-O} + \frac{1}{2}\Delta} \tag{3}$$

where the first term represents the attractive energy between Si^{4+} and the 10 electrons on O^{2-}, and the second term represents the repulsive energy between Si^{4+} and the oxygen nucleus. Equation (3) can be rearranged to a more convenient form (see van Arkel, 1949, p. 143):

$$\begin{aligned} E'_{Si-O} &= -\frac{4e2e}{d_{Si-O} - \frac{1}{2}\Delta} - \frac{4e8e}{d_{Si-O} - \frac{1}{2}\Delta} + \frac{4e8e}{d_{Si-O} + \frac{1}{2}\Delta} \\ &= -\frac{4e2e}{d_{Si-O} - \frac{1}{2}\Delta} - \frac{\Delta 4e8e}{d^2_{Si-O} - \frac{1}{4}\Delta^2}. \end{aligned} \tag{4}$$

Since Δ is usually very small relative to d_{Si-O}, the expression becomes:

$$E'_{Si-O} = -\frac{4e2e}{d_{Si-O}} - \frac{\Delta 4e8e}{d^2_{Si-O}} \tag{5}$$

where the first term is the same as the attractive energy between Si^{4+} and unpolarized O^{2-} in quartz, and the second term represents an additional attraction caused by the dipole induced in O^{2-} in the silicate.

With reference to the energy of a M^{z+} ion with respect to the polarized O^{2-} ion it is noted that the distance between M^{z+} and the center of gravity of the displaced electron cloud on O^{2-} is approximately $d_{M-O}+1/2\Delta \cos\alpha$, where α is the angle between the M—O joint and the induced dipole in O^{2-}, which in this symmetric and simple model is parallel to the Si—O joint. The distance between M^{z+} and the oxygen nucleus is approximately $d_{M-O}-1/2\Delta \cos\alpha$. The electrostatic energy of M^{z+} with respect to the oxygen dipole is thus:

$$\begin{aligned} E'_{M-O} &= -\frac{ze10e}{d_{M-O} + \frac{1}{2}\Delta\cos\alpha} + \frac{ze8e}{d_{M-O} - \frac{1}{2}\Delta\cos\alpha} \\ &= -\frac{ze2e}{d_{M-O} + \frac{1}{2}\Delta\cos\alpha} + \frac{ze8e\Delta\cos\alpha}{d^2_{M-O} - \frac{1}{4}\Delta^2\cos^2\alpha} \end{aligned} \tag{6}$$

or, if Δ is very small relative to $d_{\text{M-O}}$:

$$E'_{\text{M-O}} = -\frac{ze2e}{d_{\text{M-O}}} + \frac{ze8e\Delta\cos\alpha}{d^2_{\text{M-O}}}. \tag{7}$$

The first term is the electrostatic energy of M^{z+} with respect to unpolarized O^{2-} and thus is identical to the energy of the M—O bonds in the metal oxide. The second term represents an additional energy of the M—O link due to the dipole moment of the polarized oxygen in the silicate.

When expression (5) is compared with expression (1) it is seen that the energy of a Si—O link in the orthosilicate anion is lower than the energy of this link in quartz, provided that the field around Si^{4+} is stronger than the resultant of the fields around the m M^{z+} ions such that the electrons of O^{2-} are displaced toward Si^{4+}. Under the same conditions it is seen that the energy of the M—O link in the silicate (expression (7)) is higher than that of the same link in the metal oxide provided that $\alpha < 90°$ (so that $\cos\alpha$ is positive). *It is noted that the decrease in energy of one Si—O bond is greater than the increase in energy of one M–O bond for cations which are larger and have lower charge than Si^{4+}.* If a silicate shall form from quartz and metal oxide exothermally, the decrease in energy due to changes in all the Si—O links in a crystal must be numerically larger than the increase in energy due to changes in all the M—O links in the same crystal. In order to consider this we must count Si—O and M—O links in an orthosilicate and in equivalent amounts of quartz and metal oxide. There are 4N Si—O links in an orthosilicate of type $M_{4/z}SiO_4$ reckoned per mol Si atoms. (N is Avogadros number.) In the same silicate there are $4n/z$ N M—O links where n is the coordination number of M^{z+}, and z its charge. In an equivalent amount of SiO_2 (one mol) there also are 4N Si—O bonds; and in an equivalent amount of metal oxide there are $4n/z$ N M—O links provided that the coordination number of M^{z+} is the same as in the orthosilicate, which is actually true in many cases.

The electrostatic energy of all the M—O and Si—O links in the free oxides which are equivalent to one mol $M_{4/z}SiO_4$ is then:

$$\sum E_{\text{oxides}} = 4NE_q + \frac{4}{z}nNE_{\text{M-O}} = -4N\frac{4e2e}{d_{\text{Si-O}}} - \frac{4}{z}nN\frac{ze2e}{d_{\text{M-O}}} \tag{8}$$

(see equations (1) and (2)). The energy of the corresponding bonds in the orthosilicate, $M_{4/z}SiO_4$ is:

$$\begin{aligned}\sum E_{\text{silicate}} = 4NE'_{\text{Si-O}} + \frac{4}{z}nNE'_{\text{M-O}} &= -4N\left(\frac{4e2e}{d_{\text{Si-O}}} + \frac{4e8e\Delta}{d^2_{\text{Si-O}}}\right)\\ &\quad - 4\frac{n}{z}N\left(\frac{ze2e}{d_{\text{M-O}}} - \frac{ze8e\Delta\cos\alpha}{d^2_{\text{M-O}}}\right)\end{aligned} \tag{9}$$

where for simplicity all the M^{z+} ions which are linked to one O^{2-} ion are supposed to make the same angle, α, with the dipole of the polarized oxygen which is parallel to the O—Si joint (Fig. 1).

The difference in electrostatic bond energy between the silicate and the free oxides is then:

$$\Delta E = \sum E_{\text{silicate}} - \sum E_{\text{oxides}} = 4N\left(-\frac{32e^2\Delta}{d^2_{\text{Si-O}}} + \frac{n8e^2\Delta\cos\alpha}{d^2_{\text{M-O}}}\right). \tag{10}$$

A part of this energy will be absorbed as internal energy of the polarized oxygen ions (See for example Slater, 1951, p. 394). This absorbed energy is about one half of ΔE. Consequently the net energy change, or the heat of formation, ΔH, of one mol $M_{4/z}SiO_4$ from the free oxides becomes:

$$\Delta H = 16N\Delta e^2\left(\frac{n\cos\alpha}{d^2_{\text{M-O}}} - \frac{4}{d^2_{\text{Si-O}}}\right). \tag{11}$$

$8e\Delta$ is the induced dipole moment of the oxygen ion. The dipole moment is proportional to the strength of the field in which oxygen is situated (see Van Arkel, 1949, p. 143 ff):

$$8e\Delta = \bar{\alpha}F \tag{12}$$

where $\bar{\alpha}$ is the polarizability of O^{2-} and F is the strength of the field. The strength of the field in which O^{2-} is situated is not constant but changes with distance from Si^{4+} and from the m M^{z+} ions. For simplicity we shall consider the field in the center of oxygen as the average strength of the field which polarizes oxygen. This field is equal to the difference of the field created by Si^{4+} and the resultant field created by the m M^{z+} ions. According to elementary electrostatics the strength of this field is:

$$F = \frac{4e}{d^2_{\text{Si-O}}} - \frac{mze\cos\alpha}{d^2_{\text{M-O}}} \tag{13}$$

if all the M^{z+} ions are situated in a symmetric fashion around the oxygen ion such that α is constant (see Fig. 1). Hence:

$$8e\Delta = \bar{\alpha}\left(\frac{4e}{d^2_{\text{Si-O}}} - \frac{mze\cos\alpha}{d^2_{\text{M-O}}}\right), \tag{14}$$

which, introduced into equation (12) gives:

$$\Delta H = 2Ne^2\bar{\alpha}\left(\frac{4}{d^2_{\text{Si-O}}} - \frac{mz\cos\alpha}{d^2_{\text{M-O}}}\right)\left(\frac{n\cos\alpha}{d^2_{\text{M-O}}} - \frac{4}{d^2_{\text{Si-O}}}\right). \tag{15}$$

Now the number m, of M^{z+} ions which are attached to each oxygen is related to the coordination number, n, of the cation and to its charge z. Assume that the number of cations which are attached to one O^{2-} ion is the same for all oxygen ions in a given orthosilicate and also that all M^{z+} in the silicate have the same coordination number with respect to oxygen. In this case one can reason as follows. There are four oxygens in an orthosilicate of type $M_{4/z}SiO_4$, and there are $4/z$ M^{z+} ions each of which requires n oxygen ions in its coordination sphere. Each oxygen must then be shared among n/zM^{z+} ions, hence:

$$m = \frac{n}{z}. \tag{16}$$

This value of m can be introduced in equation (15):

$$\begin{aligned} \Delta H &= 2Ne^2\bar{\alpha}\left(\frac{4}{d^2_{\mathrm{Si-O}}} - \frac{n\cos\alpha}{d^2_{\mathrm{M-O}}}\right)\left(\frac{n\cos\alpha}{d^2_{\mathrm{M-O}}} - \frac{4}{d^2_{\mathrm{Si-O}}}\right) \\ &= -\,2Ne^2\bar{\alpha}\left(\frac{4}{d^2_{\mathrm{Si-O}}} - \frac{n\cos\alpha}{d^2_{\mathrm{M-O}}}\right)^2. \end{aligned} \tag{17}$$

The quantities in these equations are constants except n, α, and $d_{\mathrm{M-O}}$. It is perhaps surprising to find that the charge on the cation does not occur as a variable in the equation, only the radius of the cation (which is involved in the distance $d_{\mathrm{M-O}}$) and its coordination number with reference to oxygen, together with the bond-angle α. The absence of z in equation (17) will be discussed later.

It is seen that if

$$\frac{n\cos\alpha}{d^2_{\mathrm{M-O}}} \gtrless \frac{4}{d^2_{\mathrm{Si-O}}}$$

the equation becomes negative, indicating that the silicate should be stable relative to the free oxides. The larger the difference between $4/d^2_{\mathrm{Si-O}}$ and $n\cos\alpha/d^2_{\mathrm{M-O}}$ the greater the numerical value of $-\Delta H$ and hence the more stable the silicate.[3] If

$$\frac{n\cos\alpha}{d^2_{\mathrm{M-O}}} = \frac{4}{d^2_{\mathrm{Si-O}}}$$

ΔH becomes zero and the silicate is not stable except perhaps at 0°K. If

$$\frac{n\cos\alpha}{d^2_{\mathrm{M-O}}} > \frac{4}{d^2_{\mathrm{Si-O}}}$$

the resultant field of the M^{z+} ions is stronger than that of Si^{4+} such that the negative charge on O^{2-} is displaced toward the M^{z+} ions and the nucleus toward Si^{4+}. This situation is actually rare but if it occurred, a stable silicate might possibly result, because the energy change combined with the strengthening of the M—O bonds (relative to these in M-oxide) is numerically larger than the energy change combined with the weakening of the Si—O bond (relative to this in quartz). More commonly the condition exists:

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[3] Note the previous remark on the relation between free-energy and total energy.

$$\frac{n \cos \alpha}{d^2_{M-O}} < \frac{4}{d^2_{Si-O}},$$

which means that the field around Si^{4+} is the stronger and oxygen has the negative end of its dipole closest to Si^{4+}. In this case the strengthening of the Si—O bond is more important that the weakening of the M—O bonds and energy will be released when the silicates form from the oxides. This is the usual situation found in stable silicates.

It is interesting to see how the values of ΔH calculated from equation (17) compares with the empirically found stabilities of some orthosilicates as for example Be_2SiO_4; Mg_2SiO_4; γ Ca_2SiO_4; Sr_2SiO_4 and Ba_2SiO_4. In Be_2SiO_4, Be^{2+} is surrounded by 4 oxygen ($n=4$), in the other cases the cations are surrounded by 6 oxygen ($n=6$). For simplicity we shall assume that the angle α is the same for all these silicates so that all cations about an O^{2-} ion make the same angle with the dipole of the polarized oxygen. Let this angle for example be 60°. The Si—O distance is taken as 1.65Å whereas the M—O distances are considered to be the sum of the ionic radii.

Table 4 shows some of the terms of equation (17) based upon these premises together with the *relative* ΔH-values computed from equation (17). *It is seen that the trend of the calculated* ΔH *values is the same as for*

TABLE 4. CALCULATED AND MEASURED HEATS OF FORMATIONS OF ORTHOSILICATES

Silicate	Approximate cation-oxygen distances (A)	Coordination number n	$\left(\frac{4}{d^2_{Si-O}} - \frac{n \cos \alpha}{d^2_{M-O}}\right)$	Relative ΔH calculated, eq. (17) (common factor: $2Ne^2\bar{\alpha}$)	ΔH measured, kcal per mol. M_2SiO_4
Be_2SiO_4	1.66	4	$1.47-\frac{2}{2.76}$	$-.41$	-12 ± 5
Mg_2SiO_4	2.10	6	$1.47-\frac{3}{4.41}$	$-.62$	-15 ± 1
Ca_2SiO_4	2.38	6	$1.47-\frac{3}{5.66}$	$-.70$	-32.8 ± 0.5
Sr_2SiO_4	2.59	6	$1.47-\frac{3}{6.71}$	-1.04	—
Ba_2SiO_4	2.75	6	$1.47-\frac{3}{7.56}$	-1.14	-46.0 ± 7

the actually measured heats of formation. It should be emphasized, however, that the crystal model employed above is too simple to allow correct absolute ΔH values to be calculated for the various silicates. The model does lead to calculated relative heats of formation of orthosilicates that are in agreement with experimental calorimetric data.[4]

The fact that the charge on M^{z+} does not occur in equation (17) should be discussed. This is a result of the crystal model employed being too simple. However, it can be modified to account qualitatively for change of cationic charge. It is evident from geochemical observation, as well as from heat-of-formation measurements, that the charges on the cations, not only their radii and coordination number, influences the stability of the silicates (see table (1) and (2)). The reason for the charge on M^{z+} not appearing in equation (17) is essentially due to the simple picture which was employed regarding the polarization of O^{2-}. It was assumed that the electron cloud around the oxygen nucleus was a rigid construction which during polarization was displaced relative to the nucleus so that the center of gravity of the electron cloud in the polarized oxygen fell outside the nucleus thus inducing a dipole moment in O^{2-}. In this model the relative displacement of nucleus and electron cloud of O^{2-} (situated between one Si^{4+} and m M^{z+} in symmetric configuration) is given by the field of Si^{4+} minus the *resultant* field of the m M^{z+} ions. In other words this model will not respond to variable field strengths around the individual M^{z+} ions, but only to the resultant field from all of them (measured in the center of O^{2-}). It can be shown that this resultant field will be independent of the charge on each M^{z+} (as long as n and α are the same) because if the charge increases, the number of cations around each O^{2-} decreases and *vice versa*. In an orthosilicate of type $M_{4/z}\,SiO_4$ the number of cations, m, which is attached to each oxygen is determined by the charge, z, and the coordination number, n, of the cation with reference to O^{2-} by the following relation: $m = n/z$, as discussed previously. Each cation has z positive charges and the total number of positive charges carried by the m cations is: $z \cdot m = z \cdot n/z = n$ which shows that the total number of charges carried by the m cations of charge z is simply equal to the coordination number of M^{z+} relative to oxygen. Suppose, for example, that in Li_4SiO_4, Mg_2SiO_4 and in a hypothetical compound $TiSiO_4$ the cations all have coordination number 6. Then there must be 6 Li^+, 3 Mg^{2+} and 1.5 Ti^{4+} ions respectively attached to each oxygen. (This could be true for every oxygen in the crystals, but the figures given can also rep-

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[4] It should be remembered in this connection that the polarizability of an anion in a crystalline structure is not the same as its polarizability as a free ion. The polarizabilities of anions in crystals are not known, and equation (17) cannot therefore be used to calculate quantitative energy relations.

resent the average number of cations attached to each oxygen. This must evidently be the case for a hypothetical compound $TiSiO_4$—in which some oxygens may have one Ti^{4+} attached, others two Ti^{4+} if the coordination number of all Ti^{4+} is 6). This means that the number of positive charges carried by 6 Li^+, 3 Mg^2 and 1.5 Ti^{4+} is 6 in all cases. These charges are approximately at the same distance from the center of O^{2-} because the radii of Li^+, Mg^{2+} and Ti^{4+} are very nearly equal. Let also the angle α be constant. It follows then that they give the same resultant field in the center of oxygen and consequently that the 6 Li^+, the 3 Mg^{2+} and the 1.5 Ti^{4+} ions polarize O^{2-} to exactly the same extent, provided that the electron cloud around O^{2-} is displaced as a rigid body relative to the nucleus as was assumed in the model above.

If the picture of the polarized oxygen is made less simple but more in harmony with what really happens, it appears that the charge on M^{z+} is of great significance. The electron cloud around oxygen is a rather flexible construction which does not only move as a whole in response to electrostatic fields but within which adjustments take place locally in response to the fields of each individual cation attached. In other words, the electron density close to each cation is higher than normal. This means additional attraction which is going to make a configuration like Li_4OSi different in respect to energy than, for example, Mg_2OSi. It is sufficient for our qualitative model to assume that the increment of electron density (above normal) in the electron cloud of O^{2-} close to a cation, M^{z+}, is proportional to the field around the cation:

$$\eta = \frac{ze}{r^2}\mu \tag{18}$$

where η is the excess electron density in a volume with mean distance r from the cation. μ is a proportionality factor depending on the deformability of the electron cloud. (μ is not the same as the polarizability, $\bar{\alpha}$, of O^{2-} as a whole). z is the charge on the cation. The additional attraction between M^{z+} and the extra concentration of electrons close to the ion is then

$$-\frac{ze\mu}{r} = -\frac{z^2e^2\mu}{r^3} \tag{19}$$

if the repulsive energy due to overlapping of the electrons from O^{2-} and M^{z+} is disregarded. Now the deformability, μ, of the electron cloud of O^{2-} is not the same in a metal oxide and in a silicate where the strongly polarizing Si^{4+} ion pulls the electrons of O^{2-} toward the Si—O link. μ for the oxygen in most metal oxides should be somewhat larger than for oxygen bound to silicon in orthosilicates because most metal ions have less polarizing power than Si^{4+}. The difference in energy due to the kind of polarization considered above, of a M—O link in metal oxide and in silicate is:

$$\text{(20)} \qquad \frac{z^2e^2}{r^3}(\mu_{\text{ox}} - \mu_{\text{sil}})$$

where μ_{ox} is the deformability of the oxygen electron cloud in the metal oxide and μ_{sil} the deformability of the oxygen electron cloud in silicate. In most cases (when M^{z+} has less polarizing power than Si^{4+}) $\mu_{\text{sil}} < \mu_{\text{ox}}$ showing that the part of the M—O bond which is due to this kind of polarization is stronger in the oxide than in corresponding silicate. In other words *the free oxides are more stable relative to the silicates than equation (17) indicates.* It is noted that the energy difference is proportional to the square of the charge on M^{z+}. When the term above (eg. (20)) is added to equation (17) it is seen that the heat of formation of orthosilicates from the component oxides is also influenced by the charge of the cation in such a fashion that the larger the charge the less stable the silicate relative to the oxides. In other words ΔH will increase (assume smaller negative values or even be positive) with increasing z. This may be shown by an equation like the following:

$$\text{(21)} \qquad \Delta H = 2N\bar{\alpha}e^2\left(\frac{4}{d^2_{\text{Si-O}}} - \frac{n\cos\alpha}{d^2_{\text{M-O}}}\right)\left(\frac{n\cos\alpha}{d^2_{\text{M-O}}} - \frac{4}{d^2_{\text{Si-O}}}\right) + \frac{4}{z}nN\frac{z^2e^2}{r^3}(\mu_{\text{ox}} - \mu_{\text{sil}})$$

where the notations are as defined above. ($4/zn$ N is the total number of M—O links in one mol $M_{4/z}SiO_4$).

This last modification of the crystal model is then in qualitative harmony with the observed facts concerning the effect of ionic charge on the relative stabilities of the various orthosilicates. The model is certainly still too simple to permit quantitative calculations of heats of formations because factors like geometric strain in the lattices, the effect of repulsive forces on the polarization and the participation of covalent binding are neglected. On the other hand the silicate model described above explains in a simple manner the major trend of the relative stabilities of silicates of various elements.

In the following we shall see that the repulsive forces may be essential for the discussion of some stability relations of polymerized silicates.

STABILITIES OF POLYMERIZED SILICATES

It is worth noting that the maximum degree of polymerization of the silicate anion is related to type of cation (Table 2). Large and weakly charged cations are much more apt to form polymerized silicates than small and highly charged cations (only anhydrous silicates with but one kind of cation is still considered). This observation should be explainable by the crystal energy model discussed above if it is essentially correct. The fact that polymerized silicates are stable at all can be related to a varying polarizing power of the Si^{4+} ion. If silicon is surrounded by four unshared oxygens in an orthosilicate anion the polarizing power of Si^{4+} is relatively low because the electrons from all four surrounding O^{2-} ions are pulled rather close to Si^{4+} thus partly neutralizing its positive charge. In a SiO_4 tetrahedron where the silicon ion is surrounded by shared oxygens also, the electrons on the shared O^{2-} ions in the Si—O—Si bridge are not pulled very close to the Si^{4+} ion because of contrapolarization by the opposite Si^{4+} ion. *In consequence the effective polarizing power of* Si^{4+} *increases with increasing number of shared oxygen ions such that the polarization of each unshared oxygen by* Si^{4+} *is stronger the more shared oxygens that remain around the silicon ion.* The energy released by breaking a Si—O—Si bridge and making two unshared O—Si bonds, therefore, increases with increasing number of shared Si—O—Si bridges which remain around the Si ions in the polymerized silicate anions. When an orthosilicate anion forms, the energy release is low, when a metasilicate anion forms, somewhat more energy is released, and when $Si_2O_5^{2-}$—type anion forms still greater energy is released. This is clearly seen when the heat of formation from oxides of silicates with various degrees of polymerization are considered (Table 5). In this Table the heat of formation is given per a constant (two) equivalent of metal oxides in order to insure that the same number of Si—O—Si bridges are broken in all cases.

Table 5. Heats of Formation of Various Potassium Silicates from Oxides, Given in kcal per Two Equivalents[1]

Silicate	$\frac{1}{2}K_4SiO_4$	K_2SiO_3	$K_2Si_2O_5$	$K_2Si_4O_9$
$-\Delta H_{298}$	43.8±3	64.5±7	74.5±7	81.0±7

[1] Data from Kubaschewski and Evans (1951).

The decreasing stability of polymerized silicates (decreasing numerical value of ΔH) with decreasing radius and increasing charge on the cation is explainable by the same arguments as were used for the relative stabilities of the orthosilicates. However, the polymerized silicates offer a somewhat different problem: why do some of the smaller and high-charged cations form orthosilicates (or pyrosilicates) but not meta- or $Si_2O_5^{2-}$—type silicates? And why do ions which are somewhat larger and/or have less charge form ortho- and metasilicates but not $Si_2O_5^{2-}$—type silicates, leaving the most highly polymerized silicates to the largest or lowest charged cations? This is a more difficult problem and an explanation can only be suggested. The energy released when a metal oxide and quartz formed a silicate was considered essentially in two terms (1) the increased strength of the Si—O bond which releases energy, and (2) the decreased strength of the M—O bond which absorbs energy. For stable silicates the former is somewhat larger than the latter thus giving rise to exothermic formation of the silicate. Now in polymerized silicates the electron cloud of the unshared oxygen ion is pulled closer in toward Si^{4+} than in less polymerized or unpolymerized silicates, this being the chief reason why more heat is liberated when a stable polymerized silicate forms than when an orthosilicate forms with same cation. The closer to the Si^{4+} ion the electrons of O^{2-} are pulled, however, the stronger the repulsive force acting on these electrons because they penetrate deeper into the electron cloud of Si^{4+}. Hence the energy released *per distance* which the electrons on O^{2-} are pulled in toward the Si^{4+} ion is smaller and smaller the closer the electrons are pulled up to the Si^{4+} ion. The increase of energy of a M—O link *per distance* which the electrons on O^{2-} are pulled *away* from M^{z+} is proportional to the charge on M^{z+} and inversely proportional to the M—O distance. It seems possible then that if the metal cation (M^{z+}) has a relatively strong field the energy increase of the M—O bond which is connected with increasing polymerization in the silicates, is larger than the energy decrease of the Si—O bond. This would offer a qualitative explanation why orthosilicates of ions with large charge or small radii are stable but not highly polymerized silicates of such ions.

With reference to the low stability of heavy metal silicates it can readily be explained by the model presented in this paper when one remembers that these metals make ions with much stronger fields than what should be expected on the basis of their radii. Such metals (Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, etc.) behave somewhat similarly to noble gas type ions with small radius or high charge.

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