THE BONDING ENERGIES OF SOME SILICATE MINERALS

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Abstract

The bonding energies of some silicate minerals may be computed by adding the energies of the bonds between their constituent cations and oxygen, starting with the elements in the gaseous ionic state. Data from Huggins and Sun are used in the computations.

After adjusting the bonding energies of the minerals to a standard mineral cell containing 24 oxygens, they are compared for the minerals in the Bowen reaction series, for some micas and mica-like minerals found in sedimentary rocks, and for some common metamorphic minerals. Fair agreement, but not complete, between the order of bonding energy and that of mineral occurrence is observed.

It is concluded that the genesis of a mineral involves the energy balance present in its environment during formation, as well as the availability (concentration and activity) of its constituent elements, their ionic size, electronegativity, force fields, coordination and other factors.

Introduction

A mineral may be thought of as being the product of a chemical reaction which took place in a geological system; or as being the product of the response of certain elements occurring in a geological system to the energy relationships in the system at that time. The energetics of mineral genesis and stability have been considered in recent years by Fairbairn (1943), Buerger (1948), Gruner (1950), Osborn (1950), Ramberg (1952), and others. Each of these papers has treated the subject from one or more viewpoints, but still a slightly different approach may be made by utilizing data on the ionic bonding energies of simple and complex oxides (including silicates) published by Huggins and Sun (1946, 1945), and Sun and Huggins (1946).

Huggins and Sun computed the decrease in energy which follows when cations and oxygen as gaseous ions form oxides at 18° C. These energies of formation are additive for those substances where the oxygens and cations are nearest neighbors, a category which includes silicate and oxide minerals.

The energy of formation of a silicate mineral may be computed therefore, by adding the energies accruing to the individual ions—oxygen (oxides) making up the mineral. In turn, 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.

The energy values given are not the ultimate in accuracy, for as Hug-

gins and Sun (1946) point out, "we emphasize the fact that the ϵ_M values computed in this paper are only approximate average values and that theoretically they *should not* and experimentally they *do not* give accurate energies of of formation by simple additivity. Nevertheless, the approximate constancy and additivity of the ϵ_M values are useful, and comparisons of their magnitudes show correlations with the structures of atoms, crystals, and glasses which, in our opinion, are not as well shown in any other way."

Another factor of inaccuracy results as energy differences are not shown between polymorphic forms of minerals having the same chemical composition. Dickite and kaolinite, for example, possess the same computed energy values, but it is not expected that the energies are the same in those minerals because dickite is usually much better crystallized than is kaolinite. The members of the Al_2SiO_5 group of minerals, and others, are not differentiated in the energy computation.

Despite these shortcomings, the application of Huggins and Sun's data to minerals shows some interesting relationships, and stimulates further thinking on the chemistry and thermodynamics of mineral formation.

Source of Data Used

Because this paper builds directly on the work of Huggins and Sun (1946), the manner by which they obtained their fundamental data will be quoted verbatim from their article.

"For our data we use the values (Qf) of molal heats of formation (from the elements in their standard states) of the oxides and gaseous ions collected by Bichowsky and Rossini (1). These are all for a temperature of 18° C. The molal energy of formation of a compound from the simple gaseous ions we shall designate by the symbol E_i. For a simple crystalline oxide, M_mO_n, E_i is related to the Qf values according to the equation:

$$E_i[M_mO_n, \text{crystal}] = Qf[M_mO_n, \text{crystal}] - m\,Qf[M^{(2n/m)+}, \text{gas}] - n\,Qf[O^{--}, \text{gas}] - (m+n)RT \qquad (1)$$

The corresponding relations for vitreous oxides and for complex oxides (containing more than one non-oxygen element) are obvious.

It may be noted that the sign of E_i is so chosen as to make E_i greater the greater the stability of the substance, that is, the lower its actual content of energy. This convention as to the sign conforms to the convention adopted by Bichowsky and Rossini with regard to Qf values and to the universal custom in calculating and using "bond energies."

We realize that for some purposes *free energies* are of more interest than total *energies*, but calculation of the former involves complications with regard to the entropy contributions, into which we do not care to go at this time.

From the results of x-ray diffraction studies of crystals and glasses it seems certain that, with very few exceptions, each non-oxygen atom or ion, in any of the oxides we are considering, is surrounded by oxygen atoms or ions. Most of the ionic formation energy, E_i, of such a solid results from the attractions between closest neighbors—that is, from the attractions between each positive atom (Na, Ca, Si, P, $\cdots$) and the surrounding oxygens. One might expect the attraction energy between positive atoms and the surrounding shell of oxygen atoms to vary but little from compound to compound or from glass to glass. This is especially likely if the coordination number stays the same, but even with a change of coordination number the energy change should not usually be large. The energy contributions of pairs of atoms which are not closest neighbors are relatively small, and the summation of these may be assumed to be roughly the same in the compounds being considered. It is reasonable, therefore, to expect approximate additivity of energies, the E_i values being the sum of energy contributions resulting from the attraction of each positive atom for its surroundings. The calculations reported here show this to be the case. Significant departures from additivity do occur, however. In most cases they can be attributed to differences in the number or arrangement of closest neighbors.

The additivity assumption can be expressed mathematically in the following way. For a glass or compound of formula $M_m M'_{m'} M''_{m''} \cdots O_n$,

$$E_i = \sum_{M} m_{M\epsilon M}. \tag{2}$$

The m_M values are the relative numbers of metal (non-oxygen) atoms, as expressed by the formula. The ϵ_M values are constants characteristic of these elements, deduced from the experimental E_i values. Each ϵ_M is a measure of the decrease in energy when one gram-atom of the ion M and the equivalent number of oxide ions (O^{--}) are transferred from the gaseous state to an average simple or complex oxide in the solid state, in which each M has as near neighbors only oxygens and each oxygen has as near neighbors only more electropositive atoms (M, M′, M″ $\cdots$)."

Individual ϵ_M values which are listed in Table 1 are selected from a larger list in Table 1 of the article by Huggins and Sun.

Computed Energies of Silicate Minerals

To compute the molal energy of formation of forsterite, Mg_2SiO_4, for example, one simply adds:

2× 912 kg. cal. (Mg^{++})	1,824
1×3,142 kg. cal. (Si^{4+} in SiO_4)	3,142
Bonding energy, 1 mol Mg_2SiO_4	4,966 kg. cal.

The energy of formation of enstatite, $MgSiO_3$, 912+3,131, equa s 4,043.

The energy of orthoclase formation is computed:

1× 299 kg. cal. (K^+)	299
1×1,793 (Al^{3+} in silicates)	1,793
3×3,110 (Si^{4+} in SiO_2 group)	9,330
Bonding energy, 1 mol KSi_3AlO_8	11,422 kg. cal..

TABLE 1. ENERGY CONSTANTS FOR VARIOUS IONS IN SIMPLE AND COMPLEX OXIDES

Ion, M	ϵ_M in kg. cal.
Ca^{++}	839
Mg^{++}	912
Fe^{++}	919
Na^+	322
K^+	299
H^+ (in OH)	515
Ti^{4+}	2,882
Al^{+++} (in aluminates)	1,878
(in Al silicates)	1,793
Si^{4+} in $MSiO_4$	3,142
in MSi_2O_7	3,137
in M SiO_3	3,131
in M Si_4O_{11}	3,127 (computed by the writer)
in M Si_2O_5	3,123
in SiO_2	3,110

To provide a basis for comparing the energies of different mineral species, a "cell" containing uniformly 24 oxygens has been adopted. The adjusted bonding energy for the above minerals are accordingly expressed as follows:

Forsterite, as 6× 4,966 kg. cal.: 29,796 kg. cal.
Enstatite, as 8× 4,043 kg. cal.: 32,344 kg. cal.
Orthoclase, as 3×11,422 kg. cal.: 34,266 kg. cal.

The computed bonding energies, adjusted to a 24-oxygen cell, of some common silicate minerals are listed in Table 2.

MINERAL-ENERGY RELATIONSHIPS

The relation between energy and mineral genesis is not easily seen in an alphabetized table—smaller related groups should be selected for comparison. Before examining individual groups it is of interest to observe that within the silicates (and alumino-silicates), the bond which

TABLE 2. COMMON MINERALS AND THEIR ADDITIVE BONDING ENERGIES

Mineral		Additive energy of mineral formula	Bonding energy adjusted to 24 O's
Akermanite	$Ca_2Mg_2Si_2O_7$	8,864 kg. cal.	30,391 kg. cal.
Albite	$NaSi_3AlO_8$	11,445	34,335
Almandite	$Fe_3Al_2Si_3O_{12}$	15,939	31,878
Analcime	$NaSi_2AlO_6 \cdot H_2O$	9,450	32,400
Anorthite	$CaSi_2Al_2O_8$	10,645	31,935
Augite	$Ca_4Mg_2Fe_2Si_7AlO_{24}$	30,729	30,728
Biotite	$K(Mg, Fe)_3(OH)_2Si_3AlO_{10}$	30,475	30,475
Dickite	$Al_4(OH)_8Si_4O_{10}$	24,124	32,165
Diopside	$CaMg(SiO_3)_2$	8,013	32,052
Enstatite	$MgSiO_3$	4,043	32,344
Epidote	$Ca_2(Al_2Fe_1)(OH)Si_3O_{12}$	16,261	30,020
Forsterite	Mg_2SiO_4	4,966	29,796
Gehlenite	$Ca_2AlSiAlO_7$	7,593	26,890
Hornblende	$Ca_2(Mg, Fe)_5(OH)_2Si_7AlO_{22}$	31,883	31,883
Idocrase	$Ca_{10}(MgFe)(OH)_2Al_4Si_9O_{34}(OH)_2$	48,071	30,360
Muscovite	$K_2Al_4(OH)_4Si_6Al_2O_{20}$	32,494	32,494
Nepheline	$NaSiAlO_4$	5,310	31,860
Orthoclase	KSi_3AlO_8	11,422	34,266
Pyrophyllite	$Al_2(OH)_2Si_4O_{10}$	16,270	32,558
Quartz	SiO_2	3,110	37,320
Sillimanite	Al_2SiO_5	6,866	32,957
Spinel	$MgAl_2O_4$	4,668	28,008
Staurolite	$H\ Fe_2Al_9O_8Si_4O_{16}$	31,823	31,823
Talc	$Mg_3(OH)_2Si_4O_{10}$	16,258	32,516
Topaz	$Al_2(F, OH)_2SiO_4$	7,928	31,712
Tremolite	$Ca_2Mg_5(OH)_2Si_8O_{22}$	32,284	32,284

contributes most to the bonding energy, and therefore to the range in values, is the high-energy Si—O bond. A pronounced increase in bonding energy occurs in the sequence neso-<soro-<ino-<phyllo-<tectosilicate. This relationship is shown in Table 3, below. Ramberg (1952) found by another approach a parallel relationship.

The bonding energy for Si—O bonds, where 24 O's are concerned, is shown as being almost 8,500 kg. cal. greater for SiO_2 than for SiO_4^{4-}. This difference is unrealistically large for the silicate minerals, because cations will replace the (−) valences of the SiO_4 and increase the bonding energy for all groups other than SiO_2. Nevertheless, no other M—O bond energy is as large as Si—O, and therefore the tectosilicate always has the largest bonding energy within any specific M—Si—O group. Where Al occurs tetrahedrally vicarious for Si, its bonding energy is less than if all tetrahedral cations are Si; indeed, the sum of the bonding energies of vicarious tetrahedral Al with O, with that of another monovalent

TABLE 3. ENERGY SEQUENCE FROM NEOSILICATE TO TECTOSILICATE, 24 OXYGENS

Type	Factor	Adjusted bonding energy: 24 O's
Nesosilicate	$6 \cdot SiO_4$	18,852 kg. cal. plus that of 12 M^{++} bridges
Sorosilicate	$24/7 \cdot 2 \cdot Si_2O_7$	21,511 kg. cal. plus that of $10\frac{2}{7}$ M^{++} bridges
Inosilicate	$8 \cdot SiO_3$	25,048 kg. cal. plus that of 8 M^{++} bridges
Inosilicate	$\frac{24}{11} \cdot 4 \cdot Si_4O_{11}$	27,290 kg. cal. plus that of 7 M^{++} bridges and $2H^+$ (commonly)
Phyllosilicate	$\frac{24}{5} \cdot 2 \cdot Si_2O_5$	29,981 kg. cal. plus that of 6 M^{++} bridges and $4H^+$ (commonly)
Tectosilicate	$12 \cdot SiO_2$	37,320 kg. cal. plus that of 0 M^{++} bridges

cationic bond with O, is commonly less than that of unsubstituted Si—O.

The Bowen reaction series, or the Rosenbusch "decreasing basicity" series is one of neosilicate to tectosilicate. Accordingly, it might be expected that energy requirements would be the controlling factor in establishing that series, and that correspondingly the bonding energies of the minerals which actually make up the rocks exhibiting such a series would increase regularly from neosilicate to tectosilicate. This expectation appears to hold for the simple case where only one set of cations are in the minerals compared. It holds also where moderate diadochy prevails.

The uniform increase in bonding energy within mineral sequences does not follow rigorously where compound diadochy of bridging cations, and simultaneously Al for Si, come into play in some minerals but not into others. The effect of OH entering a mineral introduces complications of energy which are not understood by the writer. Minor variations in bonding energy occur between varieties of amphibole, mica, etc., so that for any stipulated energy, the formula for that individual mineral must also be expressed; a "biotite" of one composition may have more or less bonding energy than that of "hornblende." It is not surprising therefore that "exceptions" or "reversals" to the "normal order" of crystallization occur; actually their "abnormal order" may be entirely consistent with the energy balance. See Table 4 for a list of minerals from the Bowen series arranged in order of increasing bonding energy adjusted to 24 O's.

One looks askance at the low energy of formation of biotite and perhaps of augite, and at their positions higher in the table than expected. Is something wrong with the energy values; are the formulas (composition) assigned to the minerals (and from which the energies were computed) inconsistent with the true compositions of these minerals which

TABLE 4. ENERGY RELATIONSHIPS OF MINERALS IN THE BOWEN REACTION SERIES

(Adjusted to 24 O's)

Spinel, $MgAl_2O_4$—28,008

Forsterite, Mg_2SiO_4—29,796	
(Akermanite, $Ca_2MgSi_2O_7$—30,390)	
Biotite, $K(Mg, Fe)_3(OH)_2Si_3AlO_{10}$—30,475	
Augite, $Ca_4Mg_2Fe_2Si_7AlO_{24}$—30,728	
	Anorthite, $CaAl_2Si_2O_8$—31,935
Diopside, $CaMg(SiO_3)_2$—32,052	
Enstatite, $MgSiO_3$—32,344	
Hornblende, $Ca_2(Mg, Fe)_5(OH)_2Si_7AlO_{22}$—31,883	
Muscovite, $K_2Al_4(OH)_4Si_6Al_2O_{20}$—32,494	
Orthoclase, KSi_3AlO_8—34,266	
	Albite, $NaSi_3AlO_8$—34,335
Quartz, SiO_2—37,320	

actually crystallize during cooling of a magma? Or, are the values computed correctly, but is the sequence of crystallization (appearance) of minerals in a cooling magma co-controlled by a critical concentration of specific elements as well as by energy requirements. A conclusive, rigorous answer to these questions is not at hand, but it appears that the minerals (and the sequence of their appearance) which crystallize from a magma are the result of interplay, coordinated in time and space, of two factors, (1) the proper energy balance, and (2) the availability of an adequate concentration of appropriate elements.

To visualize the interplay of those last two factors it is of interest to trace the probable course of crystallization in model of a hypothetical "ordinary average" magma.

An ordinary silicate magma is rather certainly a liquid composed of —O—Si,Al—O—tetrahedra bridged, in three dimensional space, largely by alkali and alkaline earth cations, fluorine, phosphate, hydroxyl and water (Buerger, 1948), which are abundantly hydrogen-bonded (Keller and Pickett, 1954), and scantier accessories. Support is given to the above description from work done on perlite, which is a rapidly undercooled liquid magma (Keller and Pickett, 1954), and inferred from the structure proposed for artificially prepared glass (Zachariasen, 1932; Warren, 1934; Warren and Loring, 1935; Warren and Biscoe, 1938).

At the high temperature of liquidity of the magma the kinetic energy of the magma constituents is high, and the bonds within the —O-Si,Al—O—tetrahedra, and to the bridging cations, are non-uniform, changing, extended, and moderately weak.

As the magma cools it obviously loses thermal (kinetic) energy to its

surroundings. After the temperature falls to a certain point a nesosilicate like forsterite can crystallize as far as the energy balance between liquid and solid is concerned. But another condition must be met before forsterite *actually* does crystallize—a high enough ratio of Mg to SiO_4 must prevail for Mg_2SiO_4 to develop. If adequate Mg is lacking, forsterite can not crystallize although the energy balance within the magma is adequate.

As the magma continues to cool and lose energy to its surroundings, the gap widens between the reference level of gaseous ion energy and the energy in the magma. When the energy of the magma lowers to that consistent with the crystallization of enstatite, for example, it (enstatite) can then develop, provided of course that the ratio of Mg to SiO_4 is appropriate. Enstatite has a higher energy of crystallization and has higher stability than forsterite, for enstatite formation is farther removed from its gaseous ions, in terms of energy, than is olivine.

The same line of reasoning carries on downward in the scale to quartz. Always two requirements must be met for a mineral to form: (*a*) the proper energy balance, and (*b*) an adequately abundant supply of appropriate elements in the magma at that time so as to produce a solid mineral containing constituent elements in the ratio demanded by the formula. In mineral families where elements are diadochous, the element, or the distribution between vicarious elements, which enter the mineral may be expected to be governed similarly by the energy and statistical abundance of ions available.

Osborn (1950) emphasized the composition of the liquid as being more significant then the temperature in determining the type of crystal structure which will form. He related the size of cation, its coordination, and its field strength to its segregation in the crystallization history of a magma.

All of these factors are vitally important, and may modify the order of crystallization from what has been set up as "normal." When viewed in this light, the presumably anomalous positions of some minerals in the sequence in Table 3 may not be out of place so seriously after all.

Micas and Mica-Like Minerals

Bonding energies of the micas and mica-like minerals show small differences between large quantities. They are listed in Table 5.

Although the micas and mica-like minerals are listed in order of increasing bond energy, the arrangement of the bottom four has little quantitative meaning because the differences between varieties are slight in comparison to the large total energies; a slight error in the values might

TABLE 5. MICAS AND MICA-LIKE MINERALS

Mineral	Bonding energy adjusted to 24 O's
Biotite	30,475 kg. cal.
Dickite	32,165
Muscovite	32,494
Talc	32,516
Pyrophyllite	32,558

result in an interchange of position. Furthermore, the composition of dickite is the same as that of nacrite, kaolinite and halloysite, which have different stability ranges.

Muscovite and illite may have nearly the same chemical composition but their environments of genesis can differ appreciably. The same may be said of pyrophyllite and its sedimentary derivatives, the montmorillonite-group minerals.

Perhaps it is unfair to imply that the bonding energies of dickite and halloysite, or muscovite and illite, should be computed by the same procedure when it is known that halloysite and illite are not nearly so well crystallized as are dickite and muscovite.

Considerable overlap does occur in the environments of formation of these mineral groups. Dickite is found in hydrothermal ore deposits, but it also occurs in sedimentary rocks which show no proven high temperature history (Tarr and Keller, 1936). Talc likewise commonly has a hydrothermal lineage, but it forms under sedimentary evaporite conditions (Stewart, 1949). Thermal energy and temperature may not be the sole controlling energy factor in the genesis of these minerals; the chemical energy present in a concentrated evaporite environment, or the ratio of activities of reactants to those of products (as expressed in the oxidation-reduction potential equation) may influence the mineral formation drastically.

COMMON METAMORPHIC MINERALS

The bonding energies of some metamorphic minerals are listed in Table 6.

Epidote and sillimanite are outstandingly out of the positions expected for them from their occurrence in rocks. The stability of Al_2SiO_5 must certainly be modified by factors extraneous to simple bonding energy because of its trimorphic possibilities, and furthermore because it inverts to mullite and silica upon artificial heating. Why epidote should have such low bonding energy is not clear to the writer.

TABLE 6. BONDING ENERGIES OF SOME METAMORPHIC MINERALS

Mineral	Bonding energy adjusted to 24 O's
Gehlenite, $Ca_2AlSiAlO_7$	26,890
Epidote, $Ca_2(Al_2Fe)(OH)Si_3O_{12}$	30,020
Idocrase, $Ca_{10}(MgFe)(OH)_2Al_4Si_9O_{34}(OH)_2$	30,360
Biotite, $K(Mg, Fe)_3(OH)_2Si_3AlO_{10}$	30,475
Staurolite, $HFe_2Al_9O_8Si_4O_{16}$	31,823
Almandite, $Fe_3Al_2Si_3O_{12}$	31,878
Hornblende, $Ca_2(Mg, Fe)_5(OH)_2Si_7AlO_{22}$	31,883
Sillimanite, Al_2SiO_5	32,957
Orthoclase, KSi_3AlO_8	34,266
Albite, $NaSi_3AlO_8$	34,335
Quartz, SiO_2	37,320

SUMMARY

The bonding energies of some common silicate minerals have been computed by adding the bonding energies of their constituent elements, utilizing data compiled by Huggins and Sun. The notably high-energy Si—O bond dominates the bonding of the silicates.

The bonding energies of silicate mineral assemblages show fair correlation with their occurrence in rocks, but some pronounced exceptions stand out.

The approach used in these computations shows some merit, but refinements are needed to make the results more meaningful. It stresses the fact that other physical and chemical factors, such as availability (concentration and activity) of elements, their size, electronegativity, force fields, coordination, etc., enter, along with the energy balance, into the reaction from which a mineral is a product.

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