hydroxyl in the adjacent layer. The average O–OH interatomic distance is 2·89 Å, indicating the presence of hydroxyl-type bonding between the kaolin layers.

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Packing in Framework Structures*

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The topology of framework structures as described recently by Wells is considered in relation to packing coefficient. For stacked nets of regular polygons the packing decreases with the rank and proportion of the large polygon. In framework silicates, however, large polygons such as the 8-gons in feldspar are stable only in a collapsed form with diameter similar to 6-gons, and the resulting increase in packing may more than offset the topological effect. Four-connected silicate frameworks with packings appreciably greater than that of quartz are not likely.

Introduction

A general survey of possible structural arrangements in crystals was first given by Niggli (summarized in Niggli, 1941), who enumerated them on the basis of the type and arrangement of coordination polyhedra and the number of dimensions in the structural complex.

More recently Wells (1954*a*, *b*, *c*, *d*, 1955) has discussed the possible extended networks from a more strictly topological viewpoint, with particular emphasis on the proportions of polygons of various numbers of sides (here called *rank*) formed by connecting points at the centers of atoms. Wells (1954*d*) also noted the variation in packing of a framework structure with the coordination number; in terms of packing coefficient (percentage of space filled by spherical atoms; 10 times the 'packing index' of Fairbairn (1943)) representative values are:

Coordination number	Packing coefficient (%)
12	74
8	68
6	52
4	34
3	23

These considerations raise a question as to the relative importance of other variables in the packing, and in particular the possible relation of packing to the polygonal topology of the structure. In the following discussion the theoretical relations are compared with actual packings found in some known silicate framework structures. Elsewhere (Holser & Schneer, 1956) these conclusions are applied as part of a discussion of possible polymorphic transformations under the high pressures in the earth's mantle.

Packing in two-dimensional nets

We restrict the present discussion to three-dimensional 4-connected nets.† As pointed out by Wells (1954*b*, *c*), silicate or other tetrahedral frameworks that have coordination numbers 4,2 form frameworks that are topologically equivalent to these nets. One of the ways (Wells, 1954*b*) in which three-dimensional 4-connected nets may be formed is by stacking two-dimensional 3-connected nets and connecting them with additional links to each point. Wells has derived systematically 15 of these latter nets, as enumerated in Table 1 and Fig. 1 of his paper (1954*a*). Consider now the packing coefficient (in two dimensions) of these nets. Of course it will vary with the lengths and angles of the bonds, neither of which is of topological consequence. Even with the restriction of periodicity, a wide variation is possible. As a preliminary step let us form the nets from polygons which are as regular (symmetrical, with bonds of equal length) as possible, although in certain

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† The term *net* as used by Wells is not restricted to its standard crystallographic usage (International Union of Crystallography, 1952) as Wells' points are not necessarily symmetrically equivalent.

Table 1. *Packing of two-dimensional 3-connected plane nets*

Wells' No.*	Packing coefficient p_2 (%)	Fractions of polygons of each rank									
		φ_{12}	φ_{11}	φ_{10}	φ_9	φ_8	φ_7	φ_6	φ_5	φ_4	φ_3
1	60·5	—	—	—	—	—	—	1	—	—	—
15	59·3	—	—	—	—	—	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	—	—
2	58·8	—	—	—	—	—	$\frac{1}{2}$	—	$\frac{1}{2}$	—	—
8	57·2	—	—	—	—	—	$\frac{2}{3}$	—	—	$\frac{1}{3}$	—
7	57·1	—	—	—	—	$\frac{1}{3}$	—	—	$\frac{2}{3}$	—	—
14	54·5	—	—	—	—	$\frac{1}{3}$	—	$\frac{1}{3}$	—	$\frac{1}{3}$	—
3	53·9	—	—	—	—	$\frac{1}{2}$	—	—	—	$\frac{1}{2}$	—
12	53·1	—	—	—	—	$\frac{1}{3}$	$\frac{1}{3}$	—	—	—	$\frac{1}{3}$
13	53·0	—	—	—	$\frac{1}{3}$	—	—	—	$\frac{1}{3}$	$\frac{1}{3}$	—
11	51·2	—	—	—	$\frac{1}{3}$	—	—	$\frac{1}{3}$	—	—	$\frac{1}{3}$
6	49·9	—	—	$\frac{1}{3}$	—	—	—	—	—	$\frac{2}{3}$	—
10	47·8	—	—	$\frac{1}{3}$	—	—	—	—	$\frac{1}{3}$	—	$\frac{1}{3}$
4	47·5	—	—	—	$\frac{1}{2}$	—	—	—	—	—	$\frac{1}{2}$
9	43·5	—	$\frac{1}{3}$	—	—	—	—	—	—	$\frac{1}{3}$	$\frac{1}{3}$
5	39·2	$\frac{1}{3}$	—	—	—	—	—	—	—	—	$\frac{2}{3}$

* Wells, 1954*a*, p. 537, Table 1.

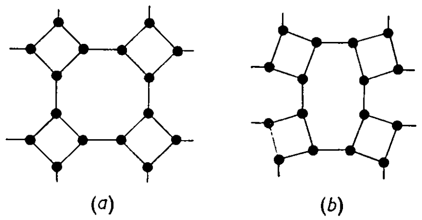

Fig. 1. 8,4-gon nets: (*a*) ideal regular form, (*b*) collapsed form in feldspar and other silicates.

nets all the polygons cannot be quite regular. In the case of those nets which can be deformed while keeping equal bond lengths, this configuration is also the one of least packing. The above restrictions reflect the *tendency* of crystal networks of similar atoms to be formed of equal, symmetrically disposed bonds.

The packing coefficient in two dimensions is

$$p_2 = 100\Sigma A_a/\Sigma A_p\,, \qquad (1)$$

where the areas of 'atoms' A_a, and of polygons A_p, are summed over some arbitrary area such as a unit mesh. If now the polygons are regular,

$$\Sigma A_a = (\pi d^2 \sum_n n\varphi_n)/4c \qquad (2)$$

and

$$\Sigma A_p = (d^2 \sum_n n\varphi_n ctn\pi/n)/4\,, \qquad (3)$$

where φ_n is the fraction of polygons of rank n and edge d, and c is the number of edges meeting in one point ('connectedness' (Wells, 1954*c*) or coordination number). Recalling Wells' (1954*a*) equation (2)

$$\sum_n n\varphi_n = 6\,, \qquad (4)$$

we get

$$p_2 = 600\pi/(c \sum_n n\varphi_n ctn n/\pi)\,. \qquad (5)$$

Applying this equation to Wells' nets, we may then relist them in order of their packing, as in Table 1.

The table in its recast form indicates the following correlation (bearing in mind the approximations made above): *the packing coefficient of a two-dimensional net decreases as the rank and proportion of the largest polygon increases,* if other factors (polygon edge, regularity, and connectedness) are held constant. Something like this might be expected intuitively, and Table 1 shows only minor deviations; but other correlations that are perhaps just as intuitively attractive are not evident in the table. The densest net (1) is also the simplest and 'most uniform' (Wells, 1954*a*), as well as the most symmetrical.

Packing in frameworks formed by stacking two-dimensional 3-connected nets

If the above two-dimensional nets were simply stacked, still keeping constant bond length, the change from circles to spheres would decrease the packing coefficients p_3, to two-thirds of the corresponding p_2's, while keeping them in the same proportions. Furthermore, when the two-dimensional nets are deformed out of a plane to conform with the normal tetrahedral bond angle, the packing coefficient is decreased by the factor $1/[1+\sin 109° \cos^2 109°] = 0{\cdot}854$. When the single sphere at a point is replaced by a cluster of 4 spheres of equal size arranged tetrahedrally along the bond directions, then the packing coefficient is increased by the factor $4\sqrt{2}/(3\sqrt{3}) = 1{\cdot}089$.

How closely do such ideal stackings approach the actual analogous crystal structures? Consider, for example, the structures of cristobalite (or tridymite) and sanidine (or other feldspars). The idealized structures are formed by stacking Wells' (1954*c*) two-dimensional nets 1 and 3 (see Fig. 1(*a*), below) respectively to form his three-dimensional nets 1 and $16C_1$ (Wells, 1954*b*). The packing coefficients (Table 2) are 38 and 33%, correlating with the ranks 8 and 6 of their major polygons. However, the actual crystal structures represent considerable deformations of the

Table 2. *Packing relations of cristobalite and sanidine structures*

Structure:	Cristobalite	Sanidine
Two-dimensional net type:	6-gon (Wells (1954*a*) net 1)	8,4-gon (Wells net 3)
Two-dimensional net (Table 1)	61%	54%
Stacked two-dimensional nets	40	36
Deformation to O–Si–O tetrahedral bond angle	35	31
Substitution of tetrahedra for points	38	33
Deformation to actual Si–O–Si bond angles	43	43
Addition of interstitial atoms	44	49
Measured (Fairbairn, 1943)	43	50

ideal in each case. In cristobalite, the Si–O–Si bonds are not 180° but 150° (Nieuwenkamp, 1935), which increases the calculated packing coefficient to 43%, comparing favorably with the measured value (Fairbairn, 1943) even when the small volume of interstitial silicon atoms is included. In sanidine a few Si–O–Si bond angles are deformed to effect a major reduction in area of the large 8-gon, as shown in Fig. 1. As a result, the packing index of the oxygen atoms is raised to almost exactly that of cristobalite. The larger packing coefficient of 50% measured for orthoclase (Fairbairn, 1943) is satisfactorily accounted for by the large interstitial ions.

The simple stacking of two-dimensional nets results in a relatively dense packing along the third dimension, perpendicular to the nets, and one may trace 4-gons and 6-gons holding the nets together in that direction. A somewhat more open structure may be derived from the stack of 4,8-gon nets by adding an extra silica tetrahedron (or an extra net point) between each pair of 4-gons along this third dimension. Zeolites such as natrolite, thomsonite, and edingtonite have structures that are equivalent to this in projection, differing only in the relative disposition of the chains composed of alternating 4-gons and single tetrahedra. Along the same direction there are 5-gons within the chains and 8-gons between them. The packing calculated for this oxygen framework is 35% with a deformation of Si–O–Si bonds similar to that in sanidine; addition of interstitial atoms (except zeolitic water) gives 47%, compared with the measured value of 46% (Fairbairn, 1943).

The structure of scapolite is also similar to that of the feldspars and zeolites. In scapolite a more open structure is attained by leaving out half of the 4-gons in every other net of the stack of 4,8-gons. The resulting oxygen packing is 42%, but the scapolite framework is more thoroughly stuffed with interstitial atoms to bring the total packing up to 52% (see Fairbairn, 1943).

Packing in other 4-connected frameworks

Four-connected networks may also be formed (Wells, 1954*b*) by stacking two-dimensional nets that are mixed 3,4-connected, the links being made at the 3-connected points of the two-dimensional nets. Wells (1954*b*) illustrated six such two-dimensional nets and their three-dimensional analogues. The packing coefficients in Table 3 were calculated by using approximate formulas similar to those used for the two-dimensional 3-connected nets. In comparing this list with that of Table 1, we see that the packing coefficients decrease with an increase in rank and proportion of the large polygon in the same way, although the packing is slightly greater in Table 3 for nets of analogous rank. The densest net (14) is of rank 4, while the lowest possible rank in 3-connected nets is 6.

Table 3. *Packing of two-dimensional* 3,4-*connected nets*

Wells' No.*	Packing coefficients p_2 (%)	Fractions of polygons of each rank					
		φ_8	φ_7	φ_6	φ_5	φ_4	φ_3
14	70·9	—	—	—	—	$\frac{1}{3}$	$\frac{2}{3}$
13	68·3	—	—	$\frac{1}{3}$	—	$\frac{2}{3}$	—
12	66·3	—	—	$\frac{1}{3}$	$\frac{1}{3}$	—	$\frac{1}{3}$
3	65·5	—	—	$\frac{1}{2}$	—	$\frac{1}{2}$	—
11	62·2	—	$\frac{1}{3}$	—	—	$\frac{1}{3}$	$\frac{1}{3}$
2	58·3	—	$\frac{1}{2}$	—	—	—	$\frac{1}{2}$
10	55·3	$\frac{1}{3}$	—	—	—	—	$\frac{2}{3}$
9	55·3	$\frac{1}{3}$	—	—	—	—	$\frac{2}{3}$

* Wells (1954*b*) uses the same number to designate both the two-dimensional 3,4-connected net and three-dimensional 4-connected net derived from it.

Stacking of two-dimensional 2,4-connected nets achieves only two new three-dimensional 4-connected nets (Wells, 1954*b*). Both are formed from different stackings of a two-dimensional net whose regular form is an edge-centered square net (8-gon) with $p_2 = 59\%$ (compared with 79% for the analogous two-dimensional 4-connected net: Wells (1954*b*) No. 1). One of the new three-dimensional nets is topologically equivalent to the silicon arrangement in quartz, but in this case the type of stacking requires that the two-dimensional net be deformed from the regular square to a 60° rhomb. By formal adherence to Wells' definitions the two-dimensional net is then 4-connected and composed of 3- and 6-gons (Wells (1954*b*) net 4*a*), with a resulting increase of p_2 to 68%. For what one might call the ideal quartz structure, this gives an oxygen packing of $p_3 = 42\%$, compared with 38% in cristobalite (Table 2). Deformation of the Si–O–Si bond angle increases the packing to 47%, compared with a value of 49% measured for low-quartz. In high-quartz, further deformation of the O–Si–O bond angle away from the ideal tetrahedral angle increases the packing still further to a measured 52%.

Wells (1954*b*) has derived 6 additional nets formed by stacking two-dimensional 2,3,4-connected nets. The latter are derived from two-dimensional 3,4-connected nets Nos. 2 and 3 (Table 3), and therefore they and the stacked three-dimensional 4-connected nets derived from them will have lower packing coefficients.

Some framework structures cannot be characterized as stacks of two-dimensional nets. Wells (1954*b*) has listed, without any systematic derivation, nine such 4-connected uniform nets that may also be described by cubic space groups. In general such nets cannot have as high packing coefficients as those formed by stacking, for the simple reason that they have large polygons extending in all three dimensions. The framework of sodalite, for example, is a three-dimensional assemblage of 4- and 6-gons, with an oxygen packing $p_3 = 30\%$. With the same deformation of Si–O–Si as in cristobalite this gives 34%, and the interstitial atoms bring it up to 46%, compared with a measured (Fairbairn, 1943) 45%.

Discussion

The packing in many three-dimensional nets is controlled by two principal variables: (1) the packing of a stack of idealized nets of regular polygons, which in turn is controlled by the polygon of highest rank; and (2) the increase of packing associated with the partial collapse of the large polygons. If a three-dimensional 4-connected net is replaced by a tetrahedral framework, a further increase in packing accompanies any bending at the tetrahedral corners.

The above survey of common silicate frameworks suggests that the second factor just about cancels the first. That is, the packing in networks based on two-dimensional 4,8-gon nets does not turn out to be much less than that in networks based on 6-gon nets, as the 8-gons are always collapsed from their regular form. The extent of this effect is shown by the following comparison of Si–Si distances *across* the large polyhedra in a number of silicates:

6-gons		8-gons	
Regular	5·03 Å	Regular	7·05 Å
Cristobalite	5·03	Apophyllite	5·20
Tridymite	5·03	Natrolite	5·13
Nephelite	5·15	Thomsonite	5·03
High-quartz	5·01	Scapolite	4·77
Low-quartz	4·89	Sanidine	4·75
		Albite	4·53

Apophyllite, a layer silicate built on a similar 8,4-gon net, is included for comparison. Although the geometries of all these nets are not strictly comparable, the data suggest that a polygon of greater rank than 6 is not stable in its regular form, but only in a collapsed form with about the same small diameter as the 6-gon. Apparently interstitial atoms do not greatly modify the polyhedra and resultant oxygen packing. The lower packing coefficients due to polygons of higher rank are evidently not realizable.

Silicate packing coefficients that are appreciably greater than those of quartz by virtue of their topology are also not to be expected, as indicated by the calculations of two-dimensional net packings. We already have in the 6-gon net of cristobalite the two-dimensional 3-connected net of greatest packing coefficient. Bond angles in the silicates restrict the formation of mixed 4-connected two-dimensional nets, although a structure may be constructed on the basis of net 3 (Table 3) with the reasonable Si–O–Si bond angle of 162° and a packing coefficient of 47%. This is still less than that in quartz. Apparently more highly packed forms of silicates, such as coesite (Coes, 1953) with $p_3 = 55\%$, must have silicate complexes with fewer dimensions or greater connectedness. These aspects of the problem will be considered elsewhere (Holser & Schneer, 1956).

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