

## Silicates with branched anions: a crystallochemically distinct class

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### Abstract

Branched single chains and rings can condense to multiple chains and rings, to layers, and to frameworks. Therefore, silicates with corner-shared tetrahedral anions are divided into: (i) unbranched silicates; (ii) branched silicates; and (iii) hybrid silicates. Branched silicate anions are strongly favored by highly electronegative cations, which cause shrinkage of the silicate chains compared to stretching from electropositive cations. The electronegativity influences the shape and topology of the silicate anions more in silicate chains than in silicate layers or even frameworks.

### Introduction

Since Machatschki (1928), Bragg (1930), and Náray-Szabó (1930), the classification of silicates has been based on condensation of corner-shared  $[\text{SiO}_4]$  tetrahedra into finite groups, rings, chains, layers, and frameworks. Recent refinement of this classification was exclusively based on the linear condensation of  $[\text{SiO}_4]$  tetrahedra (Liebau, 1972). However, a few branched anions did not fit (Liebau, 1972, Fig. 12). This paper reviews the thirty or more silicates with branched anions (Table 1), formed by sharing corners but not edges or faces.

### Definitions

$[\text{SiO}_4]$  tetrahedra that share zero, one, two, three or four corners with other  $[\text{SiO}_4]$  tetrahedra are called singular, primary, secondary, tertiary and quaternary tetrahedra, respectively. Silicate anions that contain only primary and/or secondary tetrahedra are called linear anions. These linear silicate anions are multiple tetrahedra  $[\text{Si}_m\text{O}_{3m+1}]$ , single rings  $[\text{Si}_n\text{O}_{3n}]$  and single chains  $[\text{Si}_p\text{O}_{3p}]$ . For the definition of the superscripts see Liebau (1972). So far in silicates, multiple tetrahedra have been observed with only  $m = 2$  and 3 and single rings with  $n = 3, 4, 6, 8, 9,$  and 12. In order to characterize single chains with two, three, or more tetrahedra per chain period, the periodicity of the chain,  $p$ , is expressed by the terms *zweier* single chain, *dreier* single chain, etc.: only chains with  $p = 2, 3, 4, 5, 6, 7, 9,$  and 12 have been observed. Successive linkage of linear single chains or single rings by some or all tetrahedra in their repeat unit leads to multiple chains, multiple rings, single layers,

multiple layers, and frameworks. In contrast to the branched silicate anions defined later, the linear anions and their condensation products are called unbranched silicate anions. They are marked by a  $U$  in the formula, i.e.  $U_1[\text{Si}_3\text{O}_9]$  for an unbranched *dreier* single chain like wollastonite. Additional tetrahedra can be linked to the non-terminal tetrahedra of the linear silicate anions. Since these additional tetrahedra look like branches on a stem (Fig. 1b), such anions are called branched anions. A branch may consist of one (Fig. 2a,b) or several (Fig. 2c) tetrahedra. The names open branched anion (Fig. 1b) and loop branched anion (Fig. 1c) are suggested when each branch is linked to the linear part of the anion *via* only one or more than one corner respectively. This can be expressed by superscripts  $oB$  and  $lB$  in the

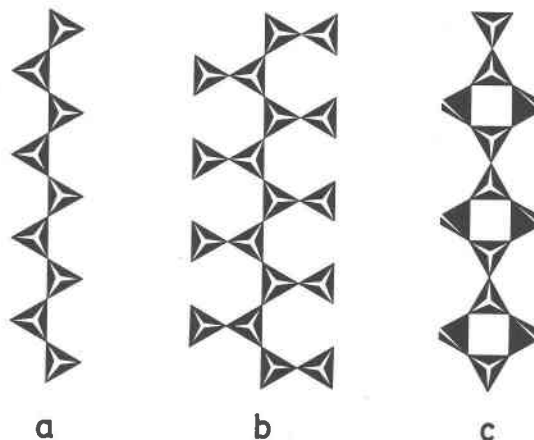


Fig. 1. Various kinds of silicate anions: (a) linear single chain; (b) open branched single chain; (c) loop branched single chain.

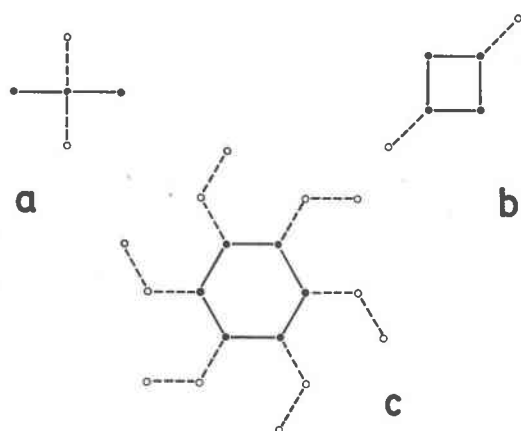
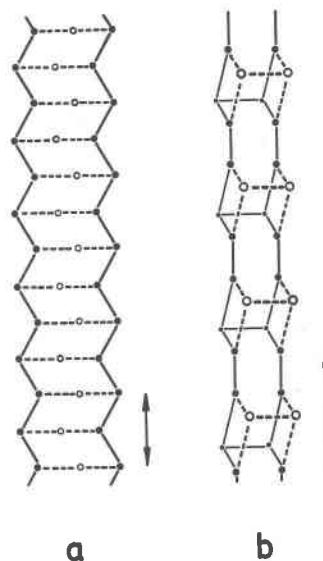


Fig. 2. Topology of the known branched 0-dimensional silicate anions: (a) open branched triple tetrahedron,  $^{ob}[Si_3O_{16}]$  (b) open branched *vierer* single ring,  $^{ob,c}[Si_6O_{18}]$  (c) open branched *sechser* single ring,  $^{ob,c}[Si_{18}O_{54}]$ . In this and subsequent figures the topology of the anions is schematic. The centers of the tetrahedra are represented by circles; the linear part of the anion (*i.e.* the "stem") by solid circles, and the branches by open circles. Connections between tetrahedra (*i.e.* shared corners) are represented by solid lines within the linear part and by broken lines within the branches.

formulae of the anions, for example,  $^{ob}[Si_6O_{18}]$  for the open-branched *vierer* single chain of aenigmatite (Fig. 3b) or  $^{lb}[Si_6O_{17}]$  for the loop-branched *vierer* single chain of lemoynite (Fig. 3c).

Branched single chains and single rings can be linked to multiple chains, multiple rings, layers, and

Fig. 4. Topology of the known branched silicate double chains: (a) open branched *zweier* double chain,  $^{ob2}[Si_6O_{18}]$  (b) loop branched *dreier* double chain,  $^{lb2}[Si_8O_{20}]$ .



frameworks in the same way as linear chains and rings. For both the branched single chains and branched single rings and their condensed products the term branched anions is suggested. The topology of the known branched double chains and single layers is shown in Figures 4 and 5 respectively. In

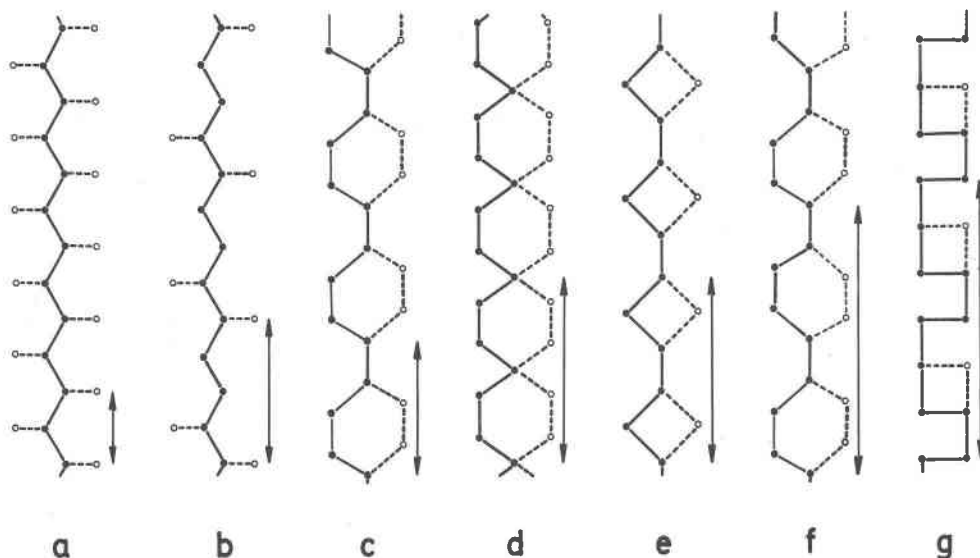


Fig. 3. Topology of the known branched silicate single chains: (a) open branched *zweier* single chain,  $^{ob1}[Si_4O_{12}]$  (b) open branched *vierer* single chain,  $^{ob1}[Si_6O_{18}]$  (c) loop branched *vierer* single chain,  $^{lb1}[Si_6O_{17}]$  (d) loop branched *sechser* single chain,  $^{lb1}[Si_6O_{22}]$  (e) loop branched *sechser* single chain,  $^{lb1}[Si_{10}O_{26}]$  (f) loop branched *achter* single chain,  $^{lb1}[Si_{12}O_{34}]$  (g) loop branched *zehner* single chain,  $^{lb1}[Si_{12}O_{34}]$ .

Table 1. Survey of the silicates with branched and hybrid anions. Cations with high electronegativity values are given in italics

<u>Branched silicate anions</u>				Fig.	Ref.
<u>Branched 0-dimensional anions</u>					
zunyite	$Al_2[AlO_4]^{OB}[Si_5O_{16}](OH,F)_{18}$	open branched triple tetrahedron		2a	1
eakerite	$Ca_2SnAl_2^{OB,C}[Si_6O_{18}](OH)_2 \cdot 2H_2O$	" " vierer single ring		2b	2
tienshanite	$KCa_3Ca_2Ba_6(Mn,Fe)_6(Ti,Nb,Ta)_6B_{12}^{OB,C}[Si_8O_{54}]_2O_{15}(OH)_2$	" " sechser " "		2c	3
<u>Branched 1-dimensional anions</u>					
astrophyllite	$KNa_2Mg_2(Fe,Mn)_5Ti_2^{OB}[Si_4O_{12}]_2(O,OH,F)_5$	open branched zweier single chain		3a	4
aenigmatite	$Na_2Fe_5Ti^{OB}[Si_6O_{18}]O_2$	" " vierer " "		3b	5
deerite	$Fe_6^{2+}Fe_3^{3+}B_4^{1B}[Si_6O_{17}]O_3(OH)_5$	loop branched vierer single chain		3c	6
howieite	$Na(Fe^{2+},Fe^{3+},Mn,Mg,Al)_{12}^{1B}[Si_6O_{17}]_2(O,OH)_{10}$	" " " " " "		3c	7
vlasovite	$Na_4Zr_2^{1B}[Si_8O_{22}]$	" " sechser " "		3e	8
lemoynite	$(Na,K)_2CaZr_2^{1B}[Si_{10}O_{26}] \cdot 5-6H_2O$	" " " " " "		3d	9
pellyite	$Ba_4Ca_2(Fe,Mg)_4^{1B}[Si_{12}O_{34}]$	" " achter " "		3f	10
nordite	$Na_4(Na,Mn)_2(Sr,Ca)_2RE_2(Zn,Mg,Fe,Mn)^{1B}[Si_{12}O_{34}]$	" " zehner " "		3g	11
bavenite	$Ca_4Be_2Al_2[Si_3O_{10}]^{OB}[Si_6O_{16}](OH)_2$	open branched zweier double chain		4a	12
fenaksite	$Na_2K_2Fe_2^{1B}[Si_8O_{20}]$	loop branched dreier double chain		4b	13
litidionite	$Na_2K_2Cu_2^{1B}[Si_8O_{20}]$	" " " " " "		4b	14
synthetic	$Na_4Cu_2^{1B}[Si_8O_{20}]$	" " " " " "		4b	15
agrellite	$Na_2Ca_4^{1B}[Si_8O_{20}]F_2$	" " " " " "		4b	16
<u>Branched 2-dimensional anions</u>					
zeophyllite	$Ca_{13}^{OB}[Si_{10}O_{28}]F_8(OH)_2 \cdot 6H_2O$	open branched vierer single layer		5a	17
meliphanite	$Ca_8(Na,Ca)_8Be_8[SiO_4]_2^{OB}[Si_{14}O_{40}]F_3$	" " " " " "		5b	18
synthetic	$Na_4^{1B}[Si_6O_{14}]$	loop branched zweier single layer		5c	19
"	$H_4^{1B}[Si_6O_{14}]$	" " " " " "		5c	20
"	$NaPr^{1B}[Si_6O_{14}]$	" " vierer " "		5d	21
"	$NaNd^{1B}[Si_6O_{14}]$	" " " " " "		5d	21
zussmanite	$KFe_{13}^{1B}[Si_{17}AlO_{42}](OH)_4$	" " fünfer " "		5e	22
leucosphenite	$Na_8Be_2Ti_4B_4^{1B}[Si_{20}O_{54}]O_6$	" " sechser " "		5f	23
<u>Branched 3-dimensional anions</u>					
leifite	$Na_6Be_2^{OB}[Si_{16}Al_2O_{39}](OH)_2 \cdot 1.5H_2O$	open branched zweier framework			24
wenkite	$(Ba,K)_4(Ca,Na)_6H_2^{OB}[(Si,Al)_{20}O_{43}][SO_4]_3 \cdot H_2O$	" " dreier " "			25
synthetic	$K_2Ce^{OB}[Si_6O_{15}]$	" " vierer " "			26
a number of zeolites, e.g.:					
natrolite	$Na_4^{1B}[Si_6Al_4O_{20}] \cdot 4H_2O$	loop branched dreier framework			27
edingtonite	$Ba_2^{1B}[Si_6Al_4O_{20}] \cdot 8H_2O$	" " " " " "			28
brewsterite	$(Sr,Ba)_2^{1B}[Si_{12}Al_4O_{32}] \cdot 10H_2O$	" " " " " "			29
dachiardite	$Na_5^{1B}[Si_{19}Al_5O_{48}] \cdot 12H_2O$	" " vierer " "			30
zeolite A	$K_{12}^{1B}[Si_{12}Al_2O_{48}] \cdot 27H_2O$	" " fünfer " "			31
thomsonite	$Na_4Ca_8^{1B}[Si_{20}Al_2O_{80}] \cdot 24H_2O$	" " sechser " "			32
<u>Hybrid silicate anions</u>					
tinaksite	$NaK_2Ca_2TiH^{1B}[Si_7O_{19}]O$	hybrid dreier double chain		6	33

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contrast, linear anions can be linked with branched ones to yield hybrid anions, whose formula may be represented by the superscript  $H$  as in the *dreier* double chain  $\text{H}_2^{21}[\text{Si}_7\text{O}_{19}]$  of tinaksite (Fig. 6), the only known member of this new group of silicates.

### Crystallochemical discussion

Is this subdivision of silicates pure formalism or is there a crystal-chemical difference between the three groups: (i) unbranched silicates, (ii) branched silicates, and (iii) hybrid silicates?

All but one (agrellite) of the silicates with 0- and 1-dimensional branched anions contain appreciable amounts of highly electronegative cations (Table 1). With increasing degree of condensation of  $[\text{SiO}_4]$  tetrahedra to layers and frameworks, the portion of branched silicates containing strongly electronegative cations appears to decrease. This observation relates the classification of silicate anions into unbranched and branched groups to the results of a recent investigation on the influence of cation properties on the shape of linear silicate single chains (Liebau, 1977). In the course of this investigation the shape of the unbranched single chains was described by the perio-

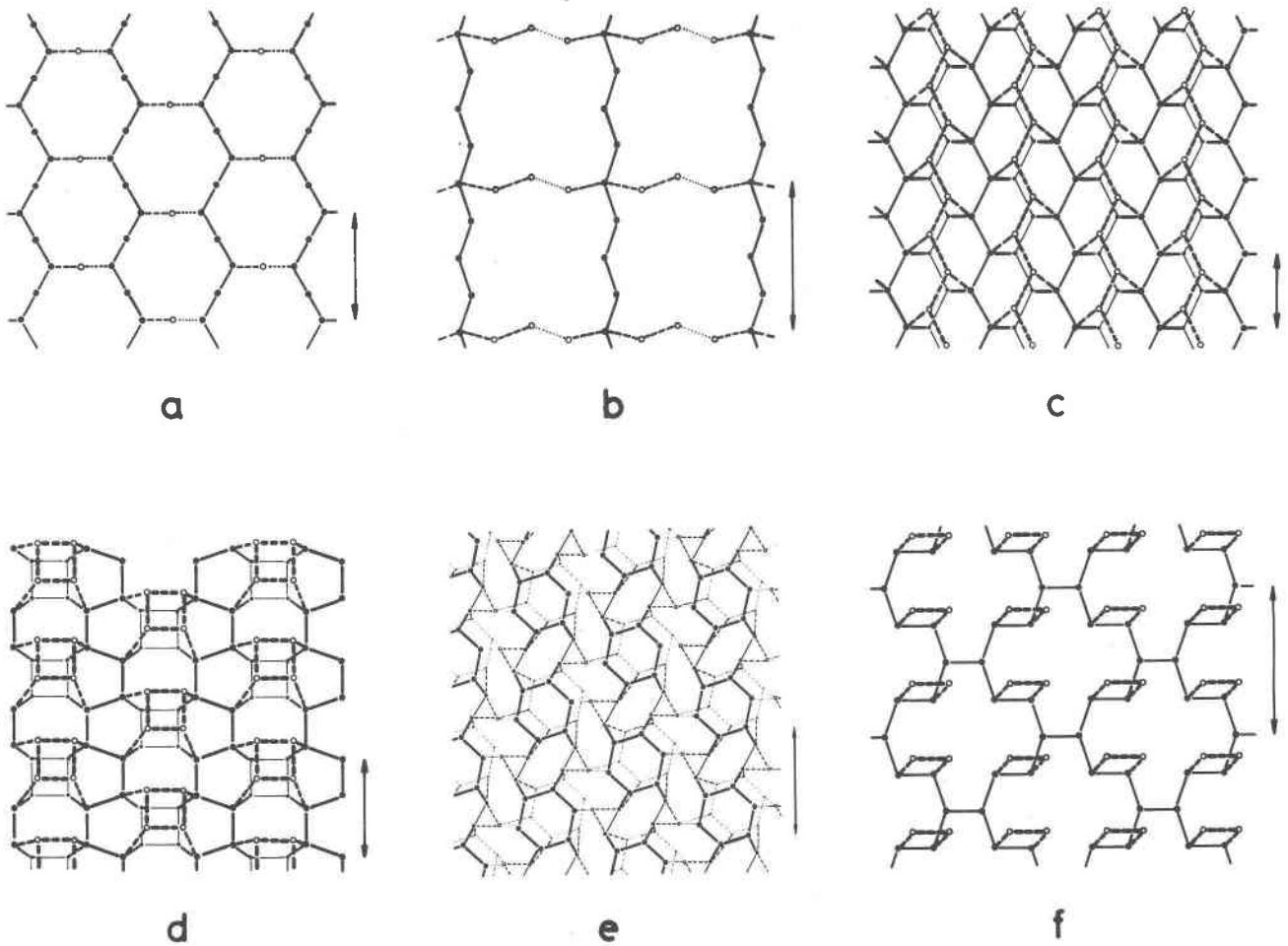


Fig. 5. Topology of the known branched silicate single layers: (a) open branched *vierer* single layer,  ${}^{oB2}[\text{Si}_{10}\text{O}_{28}]$  (b) open branched *vierer* single layer,  ${}^{oB2}[\text{Si}_{14}\text{O}_{40}]$  (c) loop branched *zweier* single layer,  ${}^{lB2}[\text{Si}_6\text{O}_{14}]$  (d) loop branched *vierer* single layer,  ${}^{lB2}[\text{Si}_6\text{O}_{14}]$  (e) loop branched *funfer* single layer,  ${}^{lB2}[\text{Si}_{17}\text{AlO}_{42}]$  (f) loop branched *sechser* single layer,  ${}^{lB2}[\text{Si}_{20}\text{O}_{54}]$ .

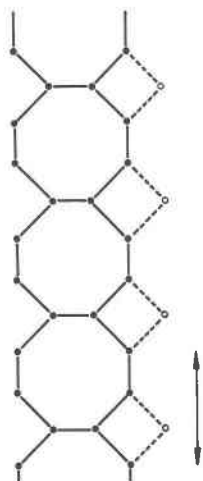


Fig. 6. Topology of the hybrid *dreier* double chain of tinaksite,  ${}^{H21}[\text{Si}_7\text{O}_{19}]$ .

dicity,  $p$ , of the chain and a stretching factor

$$f_s = \frac{l_{\text{chain}}}{l_e \times p}$$

with  $l_{\text{chain}}$  the identity period of the chain in A and  $l_e = 2.70\text{\AA}$ , the length of the edge of a  $[\text{SiO}_4]$  tetrahedron. Therefore, the stretching factor is a relative measure of the deviation from a maximum stretched chain for which  $f_s = 1.00$ . A regression analysis of the form

$$f_s = \varphi(\bar{\chi}, \bar{r}, \bar{v}, N)$$

was performed, where  $\bar{\chi}$ ,  $\bar{r}$ ,  $\bar{v}$  are the mean values of the electronegativities, the radius for coordination number 6, and the valences of the cations respectively.  $N$  is the number of different cations that exceed more than 10 percent of all cations in the chem-

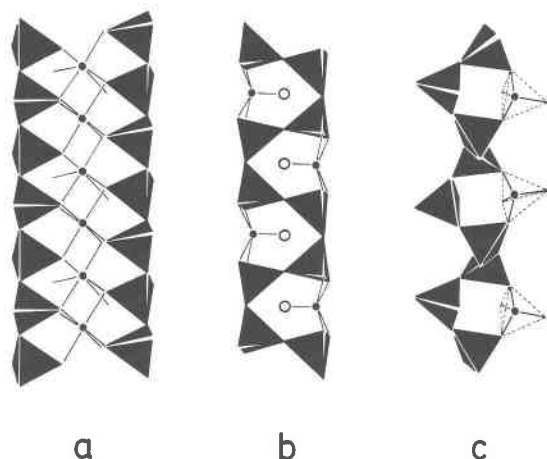


Fig. 7. Various kinds of linkages between  $[\text{SiO}_4]$  tetrahedra in chain silicates: (a) linkage in silicates with stretched linear chains by electropositive cations:  $\text{Mg}_2^{U_2}[\text{Si}_2\text{O}_6]$  (b) linkage in silicates with non-stretched linear chains by electropositive cations: haradaite  $\text{Sr}_2\text{V}_2^{U_2}[\text{Si}_4\text{O}_{12}]\text{O}_2$  (c) linkage in silicates with non-stretched linear chains by silicon: formation of loop branched single chains in vlasovite  $\text{Na}_4\text{Zr}_2^{B_1}[\text{Si}_8\text{O}_{22}]$ .

ical formula of the silicate. For silicates with even periodic chains—the vast majority of chain silicates—this regression analysis demonstrated that, with a confidence of more than 97 percent,  $f_s$  is a function of  $\bar{\chi}$ : the chains are the more stretched the lower the mean electronegativity of the cations. This is explained by the fact that cations with very low electronegativity transfer their valence electrons almost completely to the silicate anion, leading to a charge of almost two electrons per  $[\text{SiO}_4]$  tetrahedron for silicate single chains. The strong repulsion between the charges results in rather stretched silicate chains. On the other hand, cations with high electronegativities transfer fewer electrons to the silicate chain, thus reducing the repulsion forces so that the tetrahedral chains will collapse and give rise to lower values of the stretching factor,  $f_s$ .

In silicates with stretched chains the cations form bonds between tetrahedra of adjacent chains (Fig. 7a), whereas in silicates with strongly shrunken chains, a bend within a chain can either be bridged by

a cation of high electronegativity (Fig. 7b), or by another silicon atom to form a branched silicate (Fig. 7c). The observation that silicates with branched chains contain appreciable amounts of strongly electronegative cations, together with the results of the regression analysis that such electronegative cations cause a shrinkage of the chain, gives a crystallochemically plausible explanation for the existence of branched chain silicates.

The influence of the cation electronegativity on the shape of the silicate anions works for two- and three-dimensionally infinite silicate anions as well. However, since the ratio *cation:silicon* decreases from chain silicates to tectosilicates, this influence also decreases and, in fact, the portion of branched silicates not containing highly electronegative cations increases in the same order (Table 1).

In summary, from a crystal-chemical point of view the subdivision of silicates into those with unbranched, branched, and hybrid anions is reasonable, since the grouping is correlated with the electronegativity of the cations, especially in chain and layer silicates.

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