The role of cationic hydrogen in pyroxenoid crystal chemistry

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Abstract

In pyroxenoids containing cationic hydrogen [pectolite, schizolite, serandite, unnamed $Ca(Sc,Fe^{3+})H[Si_3O_9]$, synthetic $Cd_2NaH[Si_3O_9]$, nambulite, Li-hydrorhodonite, santaclaraite, and babingtonite] the identity periods of the silicate chains are approximately 0.25Å shorter than those of corresponding non-acid pyroxenoids with similar mean cation size (wollastonite, bustamite, rhodonite). This observation is interpreted as caused by the reduction of repulsive forces between $[SiO_4]$ tetrahedra of the silicate chains due to an increase of the average electronegativity of the cations when cationic hydrogen is present. This effect (which exists also in polyphosphates and probably polygermanates) is an extreme case of the general effect that anionic tetrahedral chains will be less stretched when the average electronegativity of the cations is higher, which compensates the valence of the chains. The theory explains why acid chain silicates are common in pyroxenoids but not observed in pyroxenes.

Introduction

Pyroxenoids are silicates containing unbranched single chains $\{U, {}_\infty^1\}[Si_pO_{3p}]$ with periodicities $p = 3$, 5, 7, 9, *i.e.* with an odd number of $[SiO_4]$ tetrahedra in the repeat unit of the chains. Although the pyroxenes have a crystallographic periodicity $p_{cryst} = 2$, they can be regarded as end members of the pyroxenoid series with a formal periodicity $p_{formal} = 2n + 1$ with $n \rightarrow \infty$ (Liebau, 1972).

In pyroxenes as well as in pyroxenoids cation–oxygen octahedra share edges to form octahedral slabs that can be regarded as one-dimensionally infinite parts of the hexagonal or pseudo-hexagonal octahedral layers characteristic of the hydroxides $M(OH)_2$, M = Mg, Zn, Mn, Ca, and of most of the clay minerals. Takéuchi and Koto (1977) have pointed out that, based on the structure of the octahedral slabs, two groups of pyroxenoids can be distinguished. Using the most common members of each group, wollastonite and pectolite, they named the two groups of pyroxenoids the w-p series and the p-p series, respectively. Table 1 shows that the known members of the w-p series are anhydrous while those of the p-p series contain hydrogen atoms bonded to $[SiO_4]$ tetrahedra, *i.e.* they are acid silicates.

Ohashi and Finger (1978), in their discussion of the role of octahedral cations in pyroxenoid crystal chemistry, point out that "the role of hydrogen

would be at least as important as that of the alkali atoms in making the structures of hydrous pyroxenoids distinct from those of anhydrous ones." However, since the positions of the hydrogen atoms have not yet been accurately determined, no further discussion of their crystal-chemical role was offered.

A regression analysis of 54 single-chain silicates (Liebau and Pallas, in preparation) revealed a strong negative correlation between the degree of stretching of the silicate chains, measured by a stretching factor $f_s = I_{chain}/l_e \cdot p$, and the average values $\bar{\chi}$ and $\bar{\nu}$ of the electronegativities and valences of the cations. I_{chain} is the chain period in Å, $l_e = 2.70$Å is the length of the tetrahedral edge in shattuckite, $Cu_5[Si_2O_6]_2(OH)_2$, the silicate with the most stretched chain known (Evans and Mrose, 1977), and p is the periodicity of the chain. For pyroxenes and pyroxenoids, for which $\bar{\nu}$ hardly deviates from 2, an additional positive correlation between stretching factor and the average cation radius is observed.

Observations

Table 1 gives the lattice parameter along the chain direction, I_{chain}, for the known p-p series silicates. Also given are the chain periods for those w-p series silicates which have a similar average cation radius as the p-p series silicates (hydrogen not considered). Where the acid–non-acid pairs are known, the chain

Table 1. Comparison of the chain periods of acid pyroxenoids (p-p series) with those of corresponding non-acid pyroxenoids (w-p series)

peri-odi-city	acid compounds name	formula	ref.	I_{chain}[Å]	ΔI_{chain} [Å]	I_{chain}[Å]	non-acid compounds formula	name	ref.
3	pectolite	$Ca_2NaH[Si_3O_9]$	1	7.040	0.28	7.320	$Ca_3[Si_3O_9]$	parawollastonite	2
	schizolite	$(Ca,Mn)_2NaH[Si_3O_9]$	3	6.978	0.25	7.231	$Ca_{2.35}(Mn,Fe,Mg)_{0.65}[Si_3O_9]$	Ca-bustamite	3
	serandite	$Mn_2NaH[Si_3O_9]$	4	6.889	0.20	7.091	$Ca_{0.95}(Mn,Fe,Mg)_{2.05}[Si_3O_9]$	Mn-bustamite	3
		$Ca(Sc,Fe^{3+})H[Si_3O_9]$	5	7.076					
	synthetic	$Cd_2NaH[Si_3O_9]$	6	6.980					
	synthetic	$Na_2H[P_3O_9]$	7	6.76	0.24	7.00	$Na_3[P_3O_9]$	Maddrell's salt	8
5	Li-hydro-rhodonite	$Mn_4LiH[Si_5O_{15}]$	9	12.039	0.20	12.235	$Mn_5[Si_5O_{15}]$	synthetic	10
	nambulite	$Mn_4(Na,Li)H[Si_5O_{15}]$	11	12.016	0.22	12.233	$(Mn,Fe,Mg)_{4.21}Ca_{0.79}[Si_5O_{15}]$	rhodonite	12
	santacla-raite	$Mn_4CaH[Si_5O_{15}](OH)\cdot H_2O$	13	12.001	0.23				
	babingto-nite	$Ca_2Fe^{2+}Fe^{3+}H[Si_5O_{15}]$	14 15	12.18 12.245					
	synthetic	$Cd_4LiH[Ge_5O_{15}]$	16	12.673					
	synthetic	$Cd_4NaH[Ge_5O_{15}]$	16	12.591					

References:
1 Prewitt, 1967
2 Trojer, 1968
3 Ohashi & Finger, 1978
4 Takéuchi et al., 1976
5 Mellini, 1978
6 Belokoneva et al., 1974
7 Jost, 1962
8 Jost, 1963
9 Murakami et al., 1977
10 Narita et al., 1977
11 Narita et al., 1975
12 Peacor & Niizeki, 1963
13 Ohashi & Finger, 1980
14 Kosoi, 1976
15 Araki & Zoltai, 1972
16 Simonov et al., 1978

periods of the p-p silicates are approximately 0.25Å shorter than those of the corresponding w-p silicates, independent of the periodicity of the silicate chains. The same amount of shrinkage has been observed in acid $Na_2H[P_3O_9]$ in comparison with Maddrell's salt, $Na_3[P_3O_9]$, which is isostructural with disordered wollastonite, $Ca_3[Si_3O_9]$. The period of a pyroxenoid chain consists of n double tetrahedra and a single off-set tetrahedron sticking out from the chain like a nose, adding up to $p = 2n + 1$ tetrahedra per period. Independent of the periodicity of the chains, the shrinkage of the chains in the acid compounds takes place mainly by rotation of the two tetrahedra attached to a single off-set tetrahedron. Figure 1 compares the structures of manganoan wollastonite, $(Ca,Mn)_3[Si_3O_9]$, and serandite, $(Ca,Mn)_2NaH[Si_3O_9]$, (Ohashi and Finger, 1978) as typical representatives of the two series of pyroxenoids. Whereas in the acid compounds the three tetrahedral edges designated A–A', B–B', and A'–B' in Figure 1 form an approximate open square, they form an open trapezoid in the phases containing no cationic hydrogen. In almost all the acid phases of Table 1 the presence of

hydrogen bonds A–H–B has been proposed because of short A···B distances between 2.41Å and 2.60Å or because residual electron-density maxima have been found between the atoms A and B on difference Fourier syntheses. These hydrogen bridges form the fourth sides of the squares A–A'–B'–B.

Crystal-chemical discussion

Rather than a geometric description of the differences between atomic structures of the acid and non-acid pyroxenoid phases and their isotypes, a chemical explanation is desirable. Such an explanation based on the nature of the chemical bonds would not be restricted to crystalline single-chain silicates but would also be valid for single-chain silicates in the vitreous and liquid states as well as in solution. A chemical explanation should even be applicable to corresponding silicates containing geometries other than single-chain anions. Such an explanation along very simple and general lines is offered here.

Highly electropositive cations such as Na^+, K^+, Ca^{2+}, Ba^{2+} transfer their valence electrons almost completely to the nearest anions. In silicates of such
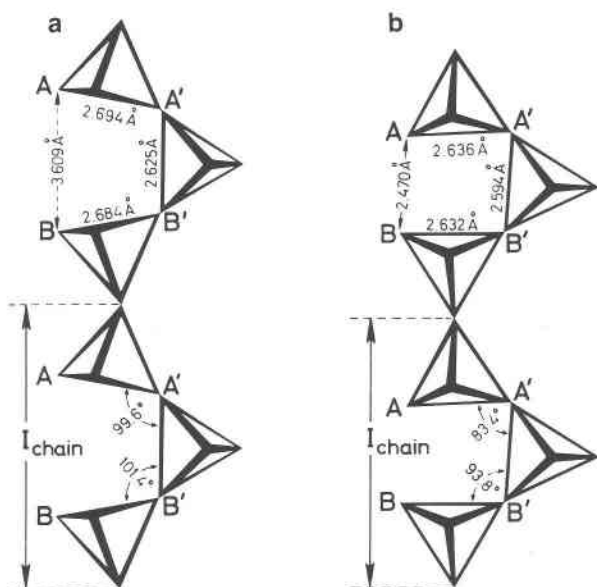
Fig. 1. Conformation of the tetrahedral single chains in corresponding acid and non-acid silicates: (a) manganoan wollastonite, $(Ca,Mn)_3[Si_3O_9]$; (b) serandite, $(Ca,Mn)_2NaH$ $[Si_3O_9]$.

cations with the general formula $M_s[Si_pO_{3p}]$ each $[SiO_4]$ tetrahedron carries a negative charge of almost two electrons. Such high negative charges cause strong repulsive forces between the tetrahedra and,

therefore, lead to a stretching of the silicate chains. As the electronegativity of the cations increases, fewer electrons are transferred from the cations to the silicate anions. This reduces the average charge per $[SiO_4]$ tetrahedron and thereby the degree of stretching of the chains.

The results of a regression analysis of single-chain silicates (Liebau and Pallas, in preparation) also support the above electrochemical explanation by giving a negative correlation between the stretching factor f_s and the average electronegativity $\bar{\chi}$ of the cations. Hydrogen with its very high electronegativity ($\chi = 2.1$) represents an extreme case for this correlation. The existence of cationic hydrogen considerably reduces the repulsive forces between silicate tetrahedra along the chain, allowing less stretched chain conformations to be favored.

It seems reasonable to assume that the reduction of negative charges on the silicate chain will be largest at those tetrahedra to which the cationic hydrogen is bonded and that the shrinkage of the chain is most pronounced in the vicinity of these tetrahedra. This is in agreement with the observations described in the last section.

Due to the general influence of electropositive cations on the repulsive forces of chain anions, the shrinkage effect of cationic hydrogen is not restricted

Table 2. Hypothetical acid and non-acid pyroxenoids and isotypic phases together with the phases from which they are predicted

peri-odi-city	predicted phase		predicted from		
	formula	I_{chain} [Å]	I_{chain} [Å]	formula	ref.
3	$Ca_2NaH[Ge_3O_9]$	7.30	7.57	$Ca_3[Ge_3O_9]$	1
	$Na_2H[As_3O_9]$	7.20	7.44	$Na_3[As_3O_9]$	2
	$Na_2H[Be_3F_9]$	6.90	7.17	$Na_3[Be_3F_9]$	1
	$(Ca,Cd)_3[Si_3O_9]$	7.23	6.98	$Cd_2NaH[Si_3O_9]$	3
	$(Ca,Sc,Fe^{3+},Na)_3[Si_3O_9]$	7.32	7.076	$Ca(Sc,Fe^{3+})H[Si_3O_9]$	4
5	$Cd_5[Ge_5O_{15}]$	12.90	12.673	$Cd_4LiH[Ge_5O_{15}]$	5
			12.591	$Cd_4NaH[Ge_5O_{15}]$	5
	$Ca_2Fe^{2+}Fe^{3+}(Li,Na)[Si_5O_{15}]$	12.45	12.2	$Ca_2Fe^{2+}Fe^{3+}H[Si_5O_{15}]$	6,7
7	$(Ca,Fe)_6(Li,Na)H[Si_7O_{21}]$	17.15	17.381	$(Ca,Fe)_7[Si_7O_{21}]$	8
	$(Ca,Mn)_6(Li,Na)H[Si_7O_{21}]$	17.20	17.45	$(Ca,Mn)_7[Si_7O_{21}]$	9

1 Liebau, 1960   4 Mellini, 1978   7 Kosoi, 1976
2 Liebau, 1956   5 Simonov et al., 1978   8 Burnham, 1971
3 Belokoneva et al.,1974 6 Araki & Zoltai, 1972   9 Liebau, 1959

to single-chain silicates but also works in other compounds such as polyphosphates, polygermanates, *etc.*

Conclusions

In general, acid hydrogen tends to form hydrogen bonds. In chain silicates these may bridge either between oxygen atoms of [SiO₄] tetrahedra of the same chain (intra-chain hydrogen bonds) or between [SiO₄] tetrahedra of different chains (inter-chain hydrogen bonds). The latter would most probably disrupt the infinite slabs of cation–oxygen polyhedra and require a major rearrangement of the structure. On the other hand, intra-chain hydrogen bonds will not have to change the cation–oxygen clusters substantially and are therefore energetically easier to achieve. The hydrogen bonds will be formed more easily if the non-acid chains are already folded so that two tetrahedra of the chain are sufficiently close that slight rotation of these tetrahedra allows formation of a hydrogen bridge between them.

This requirement is fulfilled in the structures of the non-acid pyroxenoids and their isotypic polygermanates and polyphosphates but fails for the pyroxenes and their isotypes, although their structures are closely related to those of the pyroxenoids (end members of the pyroxenoid series). In fact, pyroxenes containing cationic hydrogen have not been reported in the literature while acid pyroxenoids are quite common. In conclusion, if acid pyroxenes should be discovered, they would contain inter-chain rather than intra-chain hydrogen bonds and would be less stable than the acid pyroxenoids.

Some hypothetical pyroxenoid-type phases and their approximate chain periods are further predicted (Table 2) from the information on known pyroxenoids.

At first glance one would expect that acid analogues of multiple-chain silicates could also exist for xonotlite, $Ca_6 \{2^1_\infty\}$ $[Si_6O_{17}](OH)_2$ (Mamedov and Belov, 1956), inesite, $Ca_2Mn_7\{2^1_\infty\}$ $[Si_{10}O_{28}](OH)_2 \cdot 5H_2O$ (Wan and Ghose, 1978), canasite, $Ca_5Na_4K_2\{4^1_\infty\}$ $[Si_{12}O_{30}](OH,F)_4$ (Shiragov *et al.*, 1969), and miserite, $Ca_{10}K_2[Si_2O_7]_2\{4^1_\infty\}$ $[Si_{12}O_{30}](OH,F)_2$ (Scott, 1976). However, since in multiple chains the freedom of rotation of the tetrahedra is considerably reduced, more energy would be required to shorten a multiple chain by 0.25Å per chain period as compared with the case of single chains. Therefore, only in favorable cases could acid multiple-chain silicates with intra-chain hydrogen bridges be formed. One such case might be canasite, which has a chain period of only 7.19Å for the non-acid chains.

Note added in proof

The crystal structure of an unnamed acid silicate, $(Mn^{2+}, Mn^{3+})_5Na_{1.15}H\{B^1_\infty\}(Si_{5.5}V_{0.5})O_{18}](OH)$, has been published by R. Basso and A. Della Giusta (*Neues Jahrb. Mineral. Abh., 138,* 333–342, 1980). This silicate contains open-branched *fünfer* single chains with $I_{chain} = 11.962Å$. In agreement with the other acid pyroxenoids discussed this period is 0.27Å shorter than that of the corresponding non-acid rhodonite.

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