American Mineralogist, Volume 67, pages 1265–1272, 1982

Stereoisomerism of the pentaborate polyanion $[B_5O_{12}]^{9-}$, polymorphism and piezoelectricity in the hilgardite group of minerals: a novel class of polar borate zeolites

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Abstract

The minerals of the hilgardite group with the chemical composition $Ca_2[B_5O_9]Cl{\cdot}H_2O$ occur in a number of triclinic and monoclinic phases. In addition, an orthorhombic anhydrous phase has been synthesized. The building block of all of these structures is the pentaborate polyanion $[B_5O_{12}]^{9-}$, consisting of three borate tetrahedra and two borate triangles, which can exist in two stereoisomeric configurations (*l* or *d*). These polyanions, by sharing tetrahedral corners, form chains parallel to the *c* axis, which are connected to four such adjacent chains along the *a* and *b* axis, such that the corners of borate tetrahedra share corners of borate triangles and *vice versa*. A pseudo-tetragonal open borate framework structure is formed in this way, where the chlorine atoms and water molecules are located in straight channels parallel to the *c* axes and the calcium atoms in zigzag channels parallel to the *a* and *b* axes. The polymorphism in the hilgardite group can be explained by the various ways in which the borate chains (or layers) composed of pentaborate polyanions in *l* or *d* configurations are linked within the structure. The term "polytropism" is suggested for this particular form of polymorphism. All these structures are polar and the fairly strong piezoelectric effect in some of these phases depends on the fact that all the borate triangles may point in one direction along *a* or *b* axes. The water molecules are held by weak calcium–oxygen bonds and O–H · · · Cl type hydrogen bonds; hence, they are zeolitic in nature. Substitution of the chlorine atoms by hydroxyl ions gives rise to the tyretskite group of minerals.

Introduction

The hydrated calcium chloroborate minerals hilgardite and parahilgardite, which are monoclinic and triclinic respectively, were first described from the Choctaw Salt Dome, Iberville Parish, Louisiana by Hurlbut and Taylor (1937) and Hurlbut (1938). A different form of triclinic strontiohilgardite from Reyerhausen, Germany was subsequently described by Braitsch (1959), who noted a simple relationship among the unit cell volumes of these three phases (Table 1). Both triclinic phases (strontiohilgardite and parahilgardite) crystallize in the space group *P*1 and occur in left-handed and right-handed crystals. Hilgardite belongs to the domatic class, *m*, and crystallizes in the space group *Aa*. Braitsch (1959) called the phase relationship among these minerals a kind of "Polytropie" ("Stapelung von Links- und Rechtskristallen im Elementarbereich"). He proposed designating strontiohilgardite (which has the smallest unit cell volume of the three) 1Tc, hilgardite as 2M and parahilgardite as 3Tc, where M = monoclinic, Tc = triclinic, and 1, 2, 3 standing for the multiplicity of the unit cell volumes. The chemical composition of hilgardite and parahilgardite, originally proposed to be $Ca_8(B_6O_{11})O_4Cl_4{\cdot}4H_2O$ by Hurlbut and Taylor (1937) and Hurlbut (1938), was revised to $Ca[B_5O_8(OH)_2Cl]$ by Braitsch (1959) on the basis of the chemical composition of strontiohilgardite. The crystal structure of the synthetic orthorhombic phase of composition $Ca_2B_5O_9Br$ was described by Lloyd *et al.* (1973), who noted the similarity of the powder pattern of this phase with those of hilgardite and parahilgardite and proposed the composition $Ca_2[B_5O_9]Cl{\cdot}H_2O$ for those minerals. This composition was confirmed independently through the crystal structure determination of hilgardite and parahilgardite by Ghose and Wan (1977, 1979) and Wan

0003–004X/82/1112–1265$02.00

Table 1. Chemical and crystallographic data on hilgardite-group of minerals

Name	Chemical Composition	*a*(Å)	*b*(Å)	*c*(Å)	α(°)	β(°)	γ(°)	V(Å)^3	Z	Space Group	Reference
Unnamed	$Ca_2[B_5O_9]Cl \cdot H_2O$	6.463	6.564	6.302	61.63	118.75	105.78	205.8	1	*P1*	Rumanova et al. (1977)
Strontio-hilgardite (1Tc)	$(Ca,Sr)_2[B_5O_9]Cl \cdot H_2O$	6.608*	6.480	6.380	60.5	61.2	75.4	208	1	*P1*	Braitsch (1959)
1 Tc-Hilgardite (Cl-Tyretskite)	$(Ca,Sr)[B_5O_9]Cl \cdot H_2O$	6.656*	6.464	6.297	61.26(1)	61.58(1)	75.14(1)	205.73	1	*P1*	Hodenberg and Kühn (1977)
Tyretskite	$Ca_2[B_5O_9](OH) \cdot H_2O$	6.44	6.45	6.41	61.77	60.25	73.5	203.25	1	*P1*	Kondrat'eva (1964)
Hilgardite (2M)	$Ca_2[B_5O_9]Cl \cdot H_2O$	11.438(2)	11.318(2)	6.318(1)	90	90.06(1)	90	817.8(3)	4	*Aa*	Ghose and Wan (1977)
Parahilgardite (3Tc)	$Ca_2[B_5O_9]Cl \cdot H_2O$	17.495(4)	6.487(1)	6.313(1)	60.77(1)	79.56(1)	83.96(2)	614.8(2)	3	*P1*	Ghose and Wan (1977)
Synthetic	$Ca_2[B_5O_9]Cl$	11.26	11.13	6.63	90	90	90	830.87	4	*Pnn?*	Lloyd et al. (1973)

* *a* and *c* (α and γ) have been interchanged to keep the *c* axis close to 6.3 Å.
Notation 1Tc, 2M and 3Tc due to Braitsch (1959).

and Ghose (in prep.) and of the triclinic (1Tc) hilgardite-type phase by Rumanova *et al.* (1977).

In this paper we present a structural explanation of the polymorphic relationships among the hilgardite group of minerals, as well as the anhydrous synthetic phase, $Ca_2[B_5O_9]Cl$, which is isostructural with $Ca_2B_5O_9Br$ as described by Lloyd *et al.* (1973).

Stereoisomerism of the pentaborate polyanion

The anhydrous $[B_5O_{12}]^{9-}$ polyanion, consisting of three borate tetrahedra and two borate triangles, is the building block of the hilgardite-type borate framework structures. It was first discovered in the crystal structure of garrelsite, $NaBa_3Si_2B_7O_{16}(OH)_4$ (Ghose *et al.*, 1976). This polyanion is formed by two six-membered boron–oxygen rings nearly perpendicular to each other, which are joined through a tetrahedral boron atom. Each ring consists of a central BO_4 tetrahedron, a non-central BO_4 tetrahedron and a BO_3 triangle sharing corners (Fig. 1). The point symmetry of this polyanion is *1* in all hilgardite type phases, although the point symmetry *2* is also possible, as in garrelsite (Ghose *et al.*, 1976). There are two possible stereoisomeric configurations of this polyanion, based on placement of the borate triangle with respect to the non-central borate tetrahedron in the second ring. These two configurations are enantiomorphous with each other and are called left-handed (*l*) and right-handed (*d*)[1] (Fig. 1). Let us orient the polyanion such that the six-membered boron–oxygen ring closest to the observer is vertical and the non-central tetrahedron in this ring is above. Now, within the second ring away from the observer, if the non-central borate tetrahedron is to the right, the configuration is right-handed (*d*); if it is to the left, the configuration is left-handed (*l*). Hence, in any crystal structure with a center of symmetry and/or mirror (or glide) plane, the polyanion must exist in both configurations.[2]

In non-centrosymmetric triclinic (space group *P*1) crystals, this polyanion can exist only in the *l*- or *d*- configuration or in an odd-numbered sum of *l*- and *d*- configurations giving rise to enantiomorphous crystals as in strontiohilgardite and parahilgardite.

Crystal chemistry of the hilgardite-group of minerals

As mentioned earlier, the crystal structures of the hilgardite-group of minerals and $Ca_2B_5O_9Cl$ are characterized by an open zeolite-type three-dimensional framework, whose building block is the anhydrous pentaborate polyanion, $[B_5O_{12}]^{9-}$. In all these structures, the pentaborate polyanions form chains parallel to the *c*-axis by sharing corners of borate

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[1] These configurations were called *cis* (*l*) and *trans* (*d*) in earlier publications (*e.g.* Ghose *et al.* 1976, 1978; Ghose and Wan, 1979). The new designation supersedes the old one.

[2] Contrary to the impression given in the papers on the crystal structures of garrelsite (Ghose *et al.* 1976), ulexite (Ghose *et al.* 1978) and hilgardite (Ghose and Wan, 1979), the pentaborate polyanion exists in both *l* (*cis*) and *d* (*trans*) configurations in all these structures.

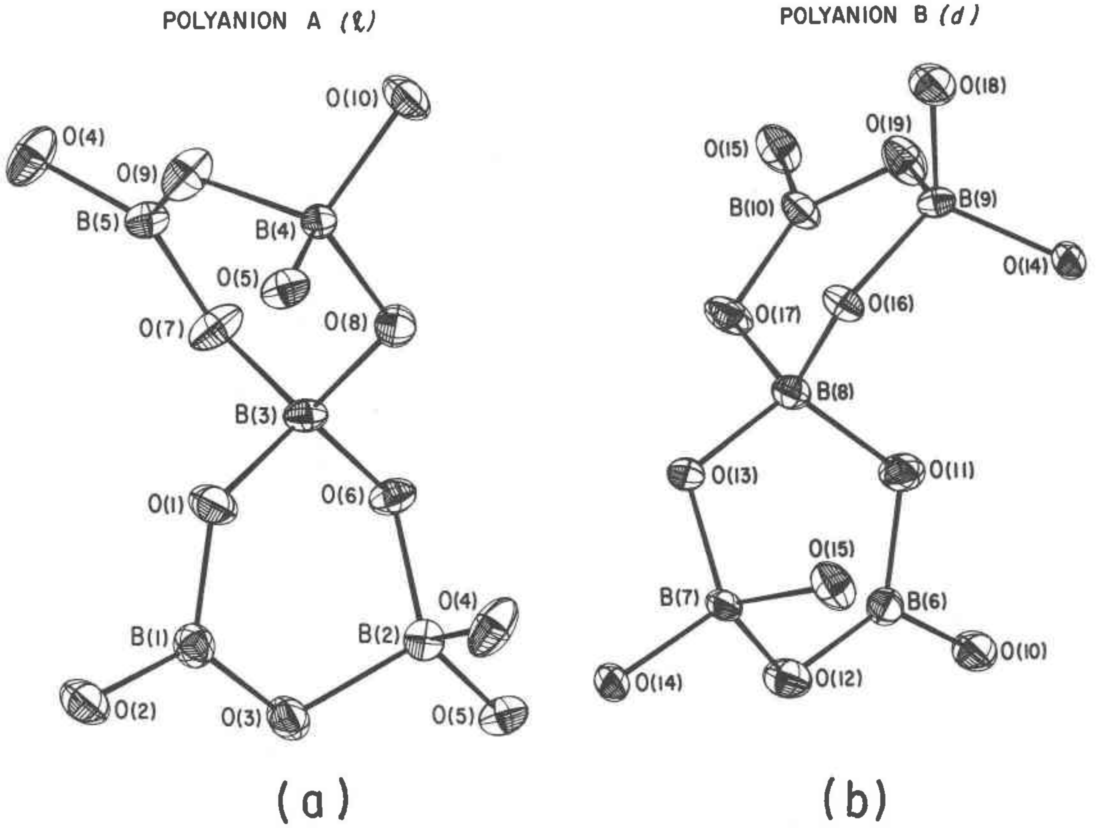


Fig. 1. Two possible stereoisomeric configurations of the pentaborate polyanion $[B_5O_{12}]^{9-}$ (a) *l* (*cis*) and (b) *d* (*trans*) as found in parahilgardite (after Wan and Ghose, in prep.).

tetrahedra with the same in adjacent polyanions, giving rise to a three-tetrahedral-repeat chain (*Dreiereinfachkette*), whose repeat distance is about 6.3Å (see Table 1 and Fig. 2). Two enantiomorphous chains are formed from pentaborate polyanions in *l* and *d* configurations. Within each chain, corners of two borate triangles may point along −**a** and −**b** directions, whereas corners of two borate tetrahedra may point along +**a** and +**b** directions. These corners are then shared with four adjacent chains, such that tetrahedral corners of one chain are shared with triangular corners of the other. An open pseudotetragonal borate framework results this way with channels parallel to *a*, *b*, an *c*-directions. In all structures, chlorine atoms and water molecules, which occur within channels parallel to *c*, alternate to form quasi-linear hydrogen-bonded chains. The water molecules, which are weakly bonded to calcium atoms, are zeolitic in nature. The calcium atoms occur in large zig-zag channels parallel to *a* and *b* directions, defined by large nine-membered rings, composed of seven borate tetrahedra and two borate triangles (Figs. 3 and 4). In such a ring, five or six nearly coplanar oxygen atoms are within 3Å of the calcium atoms. The chlorine atoms and the water molecules serve as apical ligands, completing the slightly distorted pentagonal- or hexagonal-bipyramids. All these structures are polar (with one or more polar axes) due to the fact that borate tetrahedra and borate triangles, all or in part, may point along one direction. This polarity explains the piezoelectric effect found in the hilgardite-group of minerals.

Polymorphism in the hilgardite-type phases

The structural distinction among the hilgardite-type phases lies in the two possible stereoisomeric configurations of the pentaborate polyanion and the different ways of stacking the resulting pentaborate chains or layers along the *a* and *b* axes. The simplest possibility is provided by the triclinic (1Tc) hilgardite-type phase (Rumanova *et al.*, 1977). The unit cell has the smallest dimensions and contains one formula unit per cell. Since the pentaborate

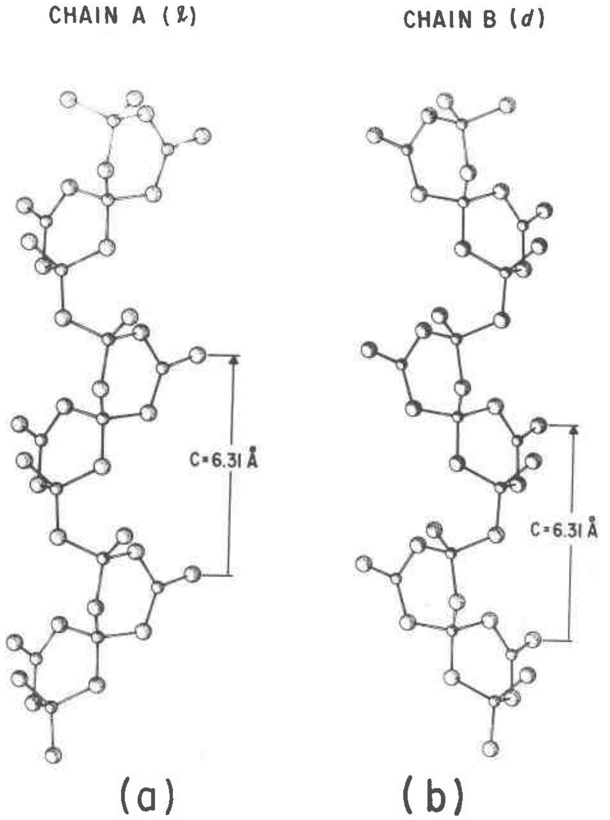
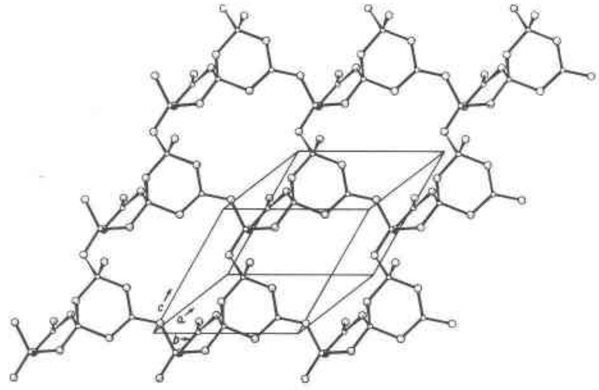


Fig. 2. Two stereochemically distinct borate chains (a) and (b) formed by pentaborate polyanions in *l* and *d* configurations respectively as found in parahilgardite (after Wan and Ghose, in prep.).

polyanion has the point symmetry *1* and all the polyanions are oriented in the same way, the space group is *P*1. In this structure, only one type of pentaborate polyanion in the *l* configuration forms crystallographic borate chains parallel to the *c* axis (Fig. 5). The crystal investigated by Rumanova *et al.* (1977) is obviously left-handed. In a right-handed crystal, the pentaborate polyanions will have the *d*-configuration. Alternatively, we can look upon the structure of 1Tc–hilgardite as formed of borate layers parallel to the (100) plane, composed of pentaborate polyanions in *l* (or *d*) configuration, which are stacked along the *a* axis.

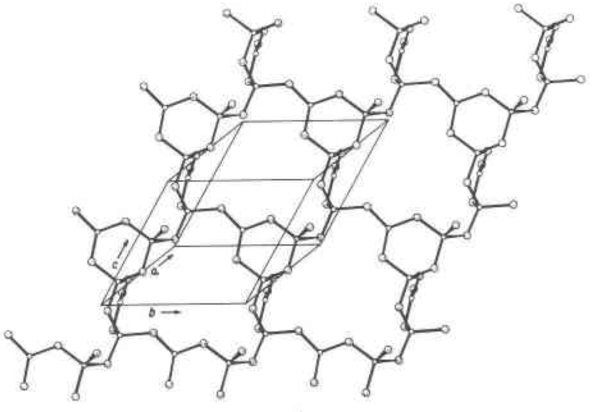
The next possibility is to stack the layers formed of pentaborate polyanions in *l* configuration alternate with those formed of polyanions in *d* configuration along the *a* axis. This structure requires an *a* glide, the *a* dimension is thereby doubled and the resulting space group is *Pa*. Although this phase has not been found so far, it leads directly to hilgardite, whose space group is *Aa*. By the A-centering, the atomic positions in the left half of the unit cell are repeated in the right half through a translation of *c*/2; by the *a*-glide, atomic positions with coordinate *x* are repeated at ½ + *x* after the mirror operation. The unit cell with space group *Aa* can be constructed from two unit cells with space group *Pa* where the (010) plane is common and the unit cells are shifted by *c*/2 in the [001] direction with respect to each other. This operation results in the *A*-centering and doubling of the *b* dimension. Such a situation is found in hilgardite (Fig. 6).

In synthetic $Ca_2B_5O_9Cl$, the *a* and *b* dimensions are the same as those in hilgardite. The structure contains pentaborate polyanions in both *l* and *d* configurations in equal proportion. The doubling of the *a* and *b* axes with respect to 1Tc–hilgardite in



LAYER A (ℓ)

(a)



LAYER B (d)

(b)

Fig. 3. Two stereoisomeric pentaborate layers, (a) and (b), formed by pentaborate polyanions in *l* and *d* configurations respectively as found in parahilgardite parallel to the (100) plane (after Wan and Ghose, in prep.).

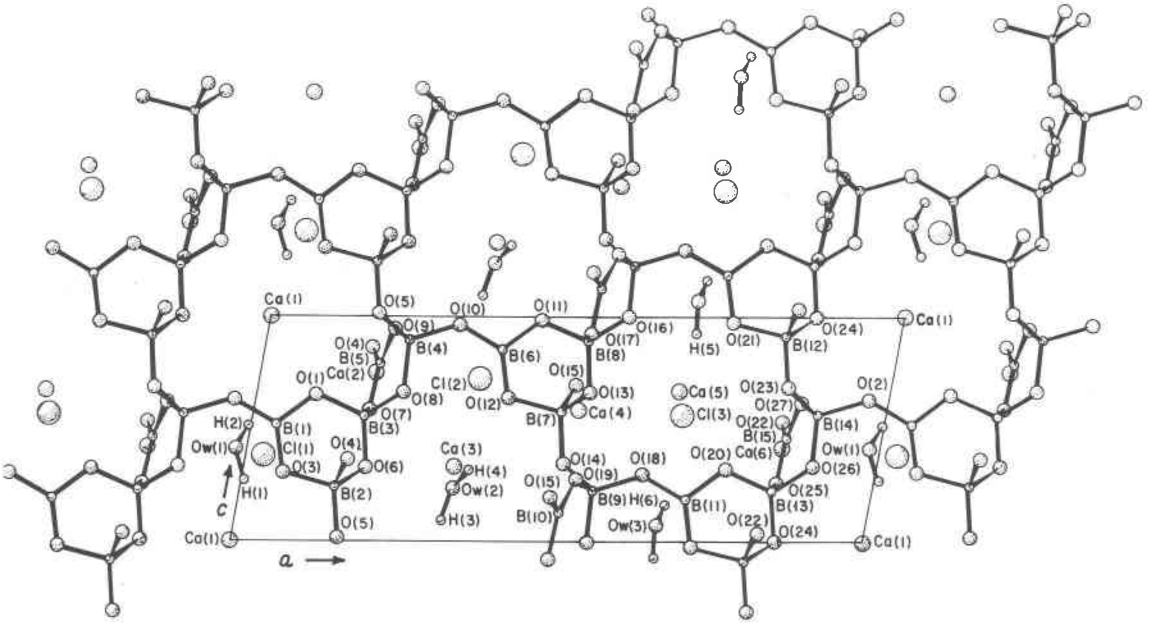


Fig. 4. A composite pentaborate layer formed of polyanions in both *l* and *d* configurations as found in parahilgardite parallel to the (010) plane (after Wan and Ghose, in prep.). Note the nine-membered borate rings, at the centers of which occur the calcium atoms.

this compound is due to the *n* glide planes normal to *a* and *b* axes (space group *Pnn*2) (Fig. 7).

Parahilgardite, whose *a* axis is three times as long as that of 1Tc–hilgardite, provides an example where three distinct borate layers, formed of pentaborate polyanions in *l*, *d* and *l* configurations respectively, are stacked along the *a* axis (Fig. 8). Since no other symmetry exists, the space group is *P*1. The parahilgardite crystal investigated by Wan and Ghose (in prep.) was a left-handed one. In a corresponding right-handed crystal, the structure will contain borate layers composed of pentaborate polyanions in *d*, *l*, *d* configurations respectively, stacked along the *a* axis.

We can conceive of an infinite variety of stacking

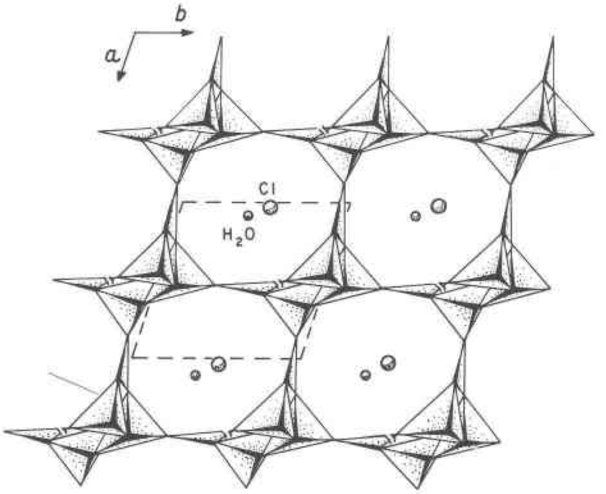


Fig. 5. Crystal structure of the 1Tc–hilgardite phase projected down the *c* axis (after Rumanova *et al.* 1977).

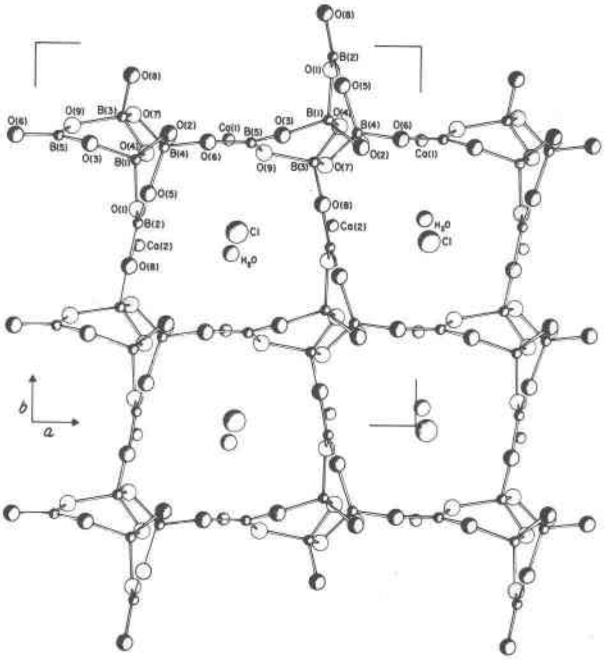


Fig. 6. Crystal structure of hilgardite projected down the *c* axis (after Ghose and Wan, 1979).

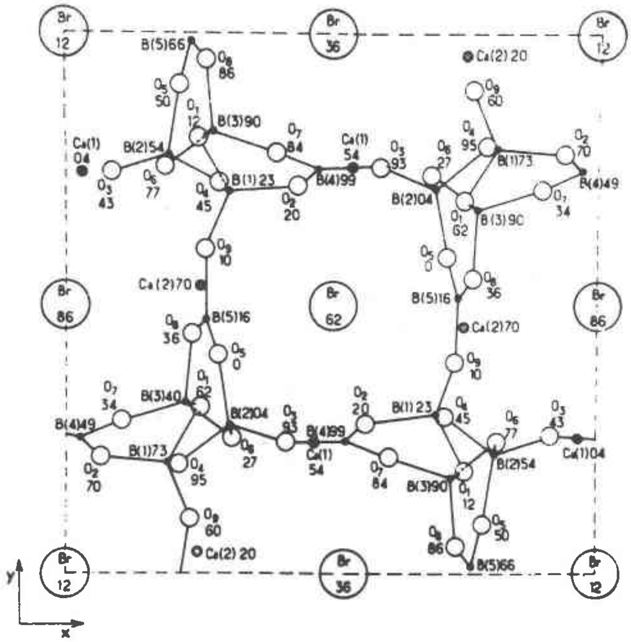


Fig. 7. Crystal structure of $Ca_2B_5O_9Br$ (isostructural with $Ca_2B_5O_9Cl$) projected down the *c* axis (after Lloyd *et al.* 1973).

sequences of borate layers, whose polyanions are in *l* and *d* configurations, resulting in a number of triclinic phases. The *a* dimensions of these phases will be na_o, where *n* is the number of distinct borate layers within a sequence along the *a* axis, and a_o is the *a* dimension of the 1Tc–hilgardite phase. Disorder in the stacking sequences of these layers is to be expected, reminiscent of the stacking disorder in biopyriboles.

Hence, the polymorphism of the hilgardite-type phases depends on the manner of stacking of the borate layers (or linking of the borate chains), where the layers (or chains) may consist of pentaborate polyanions in *l* or *d* configurations. Following Braitsch (1959), who proposed the term "Polytropie", we suggest the term "polytropism" to distinguish this phenomenon from polytypism. If we substitute the terms "Links- und Rechtskristallen", used by Braitsch (1959), by "pentaborate polyanions in *l* and *d* configurations", our explanation of the polymorphism in the hilgardite group of minerals comes very close to that offered by Braitsch. He, of course, did not have the knowledge of the crystal structures of these phases, which we do now.

Piezoelectricity in hilgardite-type phases

The crystal structures of the hilgardite-type phases offer a structural explanation of the piezoelectric effect observed in this group. Hilgardite tested for second harmonic generation gives piezoelectric signals comparable to quartz (Ghose and

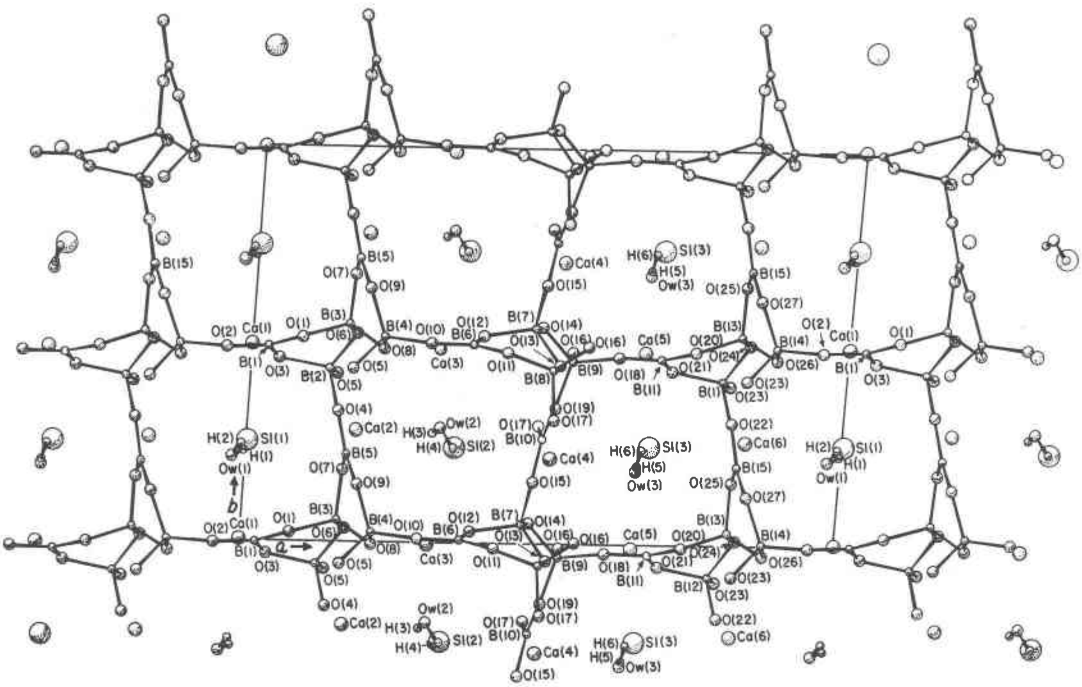


Fig. 8. Crystal structure of parahilgardite projected down the *c* axis (after Wan and Ghose, in prep.).

Wan, 1979). G. W. Pierce (see Hurlbut, 1938) noted a strong piezoelectric axis parallel or nearly parallel to the *a* axis in both hilgardite and parahilgardite. The origin of piezoelectricity in these phases lies in the way the borate tetrahedra and borate triangles are oriented within the structure. In hilgardite, due to the glide plane normal to the *b* axis, the borate triangles parallel to *b* point alternately along $+\mathbf{b}$ and $-\mathbf{b}$. Hence, piezoelectricity along *b* would be zero or nearly zero. Along the *a* axis, all the borate triangles point along the $-\mathbf{a}$ direction (Fig. 6), which explains the strong electric axis along *a*. A weak piezoelectric axis exists parallel to *c*, since all the borate tetrahedra within the borate chains point along the $-\mathbf{c}$ direction. In parahilgardite, the borate triangles within the three distinct polyanions point along $+\mathbf{b}$, $-\mathbf{b}$ and $+\mathbf{b}$ directions, whereas all the borate triangles along the *a* axis point along $-\mathbf{a}$ (Fig. 8). Hence, a strong piezoelectric axis along *a* and a weaker one along *b* are expected, which is in accordance with the experimental observation. The piezoelectric effects in 1Tc–hilgardite and $Ca_2B_5O_9Cl$ have not been measured. However, on structural grounds, strong piezoelectric axes parallel to *a* and *b* are to be expected in 1Tc–hilgardite, since the borate triangles along these axes point to $-\mathbf{a}$ and $-\mathbf{b}$ (Fig. 5). In the corresponding right-handed crystals of parahilgardite and 1Tc–hilgardite, the orientation of the borate triangles will be reversed, along with the polarity of the piezoelectric effect; however, the magnitude of the effect will remain the same. In $Ca_2B_5O_9Cl$, due to the presence of *n* glide planes normal to the *a* and *b* axes, the borate triangles point alternately along $+\mathbf{a}$ and $-\mathbf{a}$, as well as, along $+\mathbf{b}$ and $-\mathbf{b}$ (Fig. 7). Hence, in this compound, the piezoelectric effect along *a* and *b* axes would be zero or nearly zero. From such an analysis, it appears that 1Tc–hilgardite will show the strongest piezoelectric effect in this group. An experimental determination of the piezoelectric effect in this phase would be highly desirable.

Cl $\rightleftarrows$ OH substitution in hilgardite and the chemical composition of tyretskite

The unit cell dimensions of tyretskite originally described by Kondrat'eva (1964), are very close to those of 1Tc–strontiohilgardite (Table 1). On the basis of the chemical composition of strontiohilgardite (Braitsch, 1959), the composition of tyretskite, suggested to be $Ca_3B_8O_{13}(OH)_4$ by Kondrat'eva, was revised to be $Ca_2[B_5O_8(OH)_2]OH$ by Davies and Machin (1968). In view of the crystal structures of the hilgardite group of minerals, the correct chemical composition of tyretskite should be $Ca_2[B_5O_9](OH){\cdot}H_2O$. Tyretskite, which is the hydroxyl analog of 1Tc–hilgardite, should also exist in other monoclinic and triclinic modifications. The hydroxyl ions, along with the water molecules, must occur in open channels parallel to the *c* axes as quasi-linear hydrogen bonded chains in all these phases.

Conclusions

A new type of polymorphism (called "polytropism") is displayed by the hilgardite-type pentaborate phases, based on the two stereoisomers of the pentaborate polyanion $[B_5O_{12}]^{9-}$, and the different ways of linking these polyanions into chains or layers to give rise to open polar pseudo-tetragonal framework structures. All these structures are zeolitic in nature, where the chlorine atoms and the water molecules occur in large channels parallel to the *c* axes. The piezoelectricity in these phases can be explained principally on the basis of the orientation of the borate triangles along the *a* and *b* axes. Hence, they can be considered a novel class of polar borate zeolites.

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Manuscript received, February 11, 1982;
accepted for publication, May 10, 1982.