

Mysterious and changing...

TOURMALINE

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Introduction



Fig. 1 – Elbaite –San Piero, Elba Island, Tuscany, Italy. Coll. & © R. Warin.

Blooming at the end of the crystallization of pegmatites, tourmaline is multiple, fascinating and mysterious. Its crystallochemistry is varied and complex, so the amateur understands it with difficulty. Its prismatic, but often rounded appearance, and its captivating and changing colors seduce as much the visitor of the exhibitions or other shows than its composition disarms the systematic collector. It remains difficult to name it precisely to the point that it requires a crystallochemical analysis to clarify its identity. Even its chemical formula is a puzzle. It takes almost a full line to write it.

To remember its composition by heart asks for more than a single mnemonic trick or, alternatively, this requires a careful deep thought! To tell the truth, there are more than two dozen tourmalines, gathered in the Tourmaline Supergroup. But ancient usage has defined poorly defined varieties, based mainly on the hues of the crystal. Since gemstone tourmaline is a fine stone, gemologists often use this vernacular nomenclature, conveyed by usage. The rubellite is red and the indicolite is blue while the verdelite is green (often dark).



Fig. 2 – Elbaite, herderite - Pederneira Mine, Sao José da Safira, Minas Gerais, Brazil, found in 2014 – Sainte-Marie-aux-Mines Show 2018 © R. Warin.

The Tourmaline Supergroup

This group is so vast that it occupies almost two pages of Fleisher's Glossary (2014). The reader will refer to this lexicon to find its chemical formulas. Tourmalines belong to the family of cyclosilicates, whose characterization is the cyclic sequence of several $[\text{SiO}_4]$ groups. In this case, the cyclic silicate anion of tourmalines connects 6 $[\text{SiO}_4]$ tetrahedra.

This polymerization leads to an anion of formula $(\text{Si}_6\text{O}_{18})^{12-}$ centered on the vertical ternary axis c. These anionic planes are perpendicular to the c axis and the upper face is indexed (0001). Another essential element for the "tourmalinization" of silicates (for example, quartz, feldspar and micas in granites) is the presence of boron by a metasomatism process. Boron is supplied by the hydrothermal fluids in the ends of crystallizations of acid magmas producing granites. The presence of boron is often possible because it is a lithophilic element. Tourmaline is therefore also built on planes made of plane $(\text{BO}_3)^{3-}$ anions alternating with the coplanar cyclosilicates rings $(\text{Si}_6\text{O}_{18})^{12-}$. The structure accepts 3 triangular anions $(\text{BO}_3)^{3-}$ per ring $(\text{Si}_6\text{O}_{18})^{12-}$. **The general formula will therefore always contain the anionic group $[(\text{BO}_3)_3^{3-} (\text{Si}_6\text{O}_{18})^{12-}]^{21-}$.**

All these negative charges are obviously compensated by positive charges introduced by various cations. And it is here that the whole variety of substitution appears, giving free course to the very great fantasy of chance at the end of the crystallizations of pegmatites. Tourmaline is considered as the garbage can of pegmatites, accepting chemical elements refused by other crystalline structures.

This anionic lasagna is neutralized by 3 types of cations: X, Y and Z, with:

X = Na^+ and more rarely, Ca^{2+} .

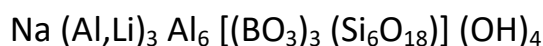
Y = Li^+ , Mg^{2+} , Fe^{2+} , Fe^{3+} , Mn^{3+} , Cr^{3+} , Al^{3+} , etc.

Z = Al^{3+} , Fe^{3+} , Cr^{3+} , V^{3+} , etc.

Since the electrical neutrality is still not completely obtained, the addition of additional small anions such as OH^- , F^- , O^{2-} is necessary. We therefore arrive at the classic general formula:



And for example, elbaite has the formula:



Cations size is also decisive for their insertion into the cavities left between the various sheets of the anionic structure. Geometric illustrations will enhance the reader representation of the situation. When the general structure of tourmaline is understood, it becomes easier to see the insertion volumes for left for the cations. Anecdotally, when I was young, the extended formula of tourmaline was sometimes required by a professor wishing to put an end to the examination... To better perceive below the main characteristics of such a

dense, while very ordered, cluster of varied atoms, the complexity of the following drawings will increase gradually.

Cristallochemistry

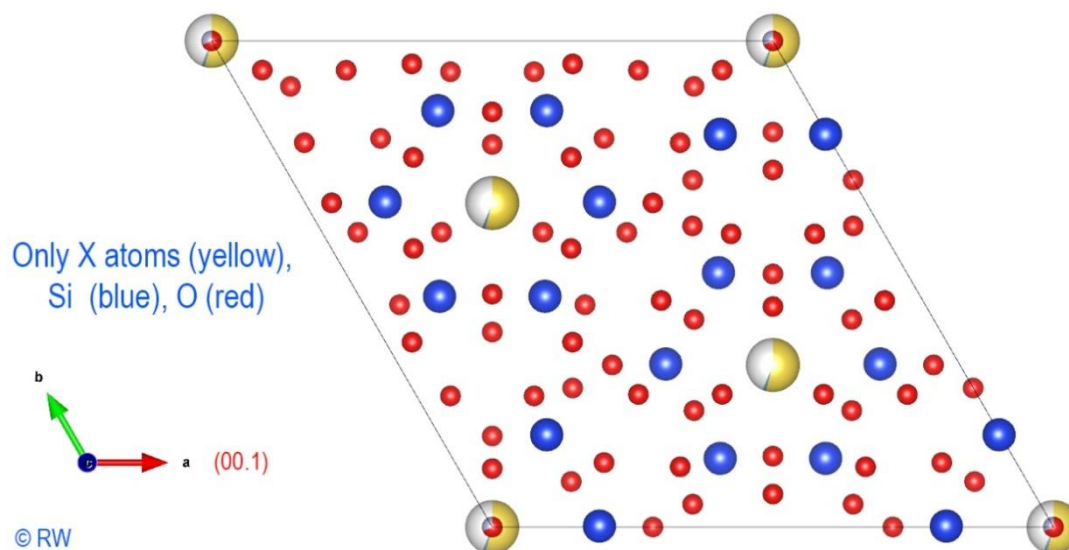


Fig. 3 – Elbaite – Perpendicular section to the vertical "c" axis without boron or aluminum atoms. © R. W.

A first structural sketch of tourmaline, expressed in the case of elbaite, is shown in the figure (Fig. 3). To simplify the scheme, boron and aluminum atoms have been omitted. Only the X atoms (yellow), Si (blue) and O (red) remain. Thus the hexagonal ring of the anion $(\text{Si}_6\text{O}_{18})^{12-}$ appears clearly, highlighting the cyclic nature of the cyclosilicate anion. The vertical ternary "c" axis is centered perpendicular to this cycle. This figure is a projection and all the atoms are not in the same plane. An upcoming figure will show the expanded structure after a rotation of the drawing.

Now, let's add boron atoms (Fig. 4). They form the borate anions $(\text{BO}_3)^{3-}$ planes. They are placed in the center of three O atoms and complete the anionic layer. The addition of Al^{3+} cations is shown in the following drawing (Fig. 5). Readability is getting lower and the discernment of atomic associations becomes more difficult. It should be noted that the symmetry of the structure is preserved in its slightest details. It remains possible to emphasize the cyclosilicate character by selectively drawing the silicon polyhedra (Fig. 6).

The spatial structure of tourmaline is useful in more than one respect. It confirms the absence of a plan of weakness that would favor a cleavage, since

we observe that its fracture is conchoidal. But there is another property that is remarkably highlighted: tourmaline has a low symmetry since it belongs to the rhombohedral $R\bar{3}m$ class. Unit cell parameters vary by species between:

$a = 15.81 - 16.10 \text{ \AA}$ $c = 7.09 - 7.25 \text{ \AA}$ $Z = 3$
 hardness = 7.5 very bad cleavages on $\{11.0\}$ et $\{10.1\}$.
 Very rare twins on $\{10.1\}$ and $\{40.1\}$.

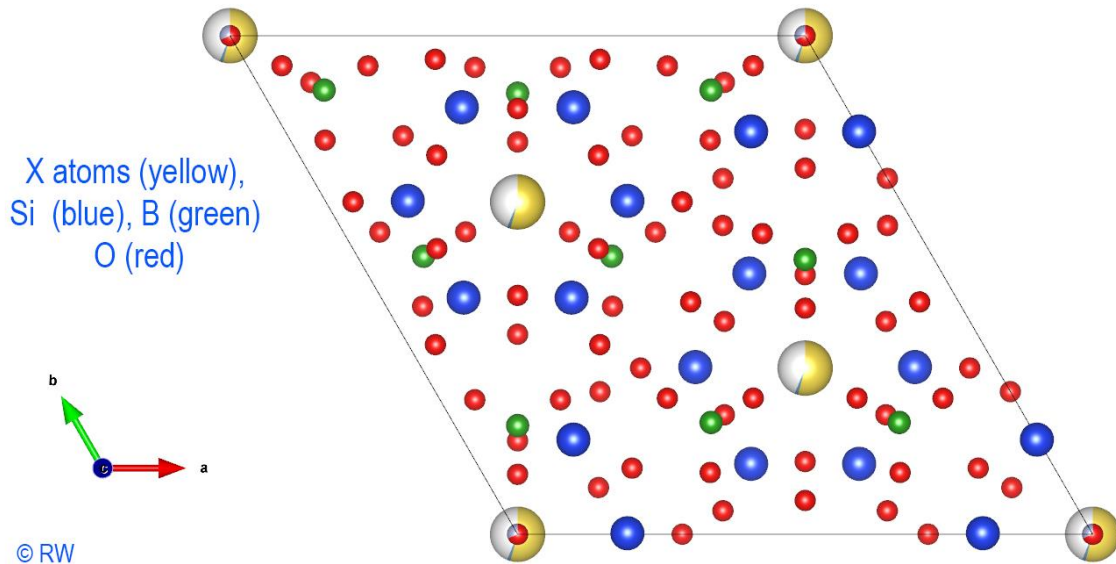


Fig. 4 – Elbaite – Perpendicular section to « c » axis without Al atoms. © R.W.

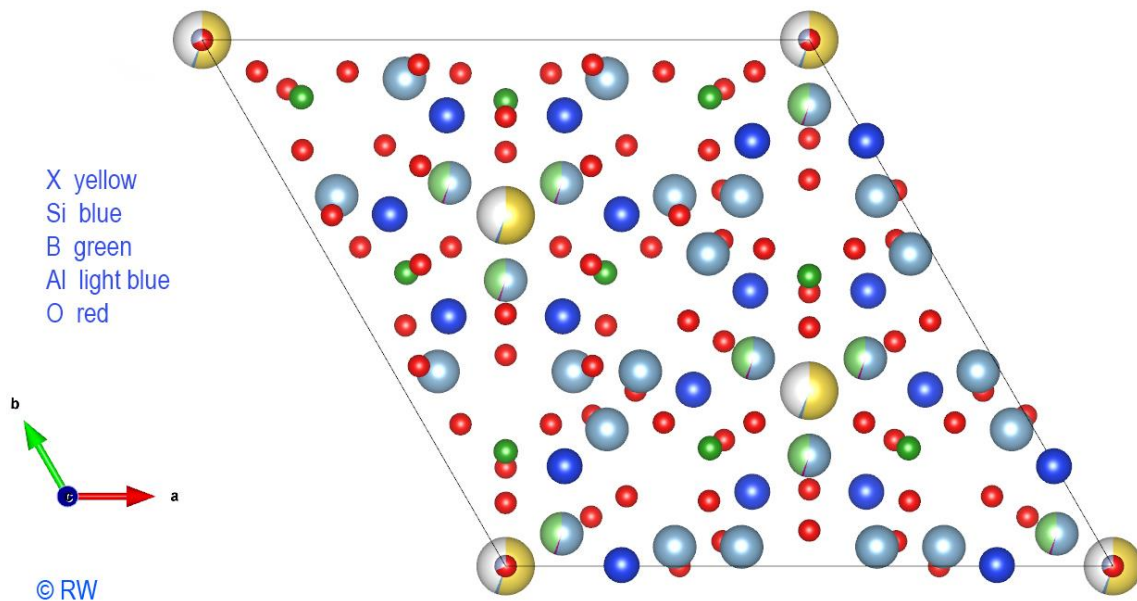


Fig. 5 – Elbaite – Perpendicular section to the vertical "c" axis.
 There are no more erased ions. © R.W.

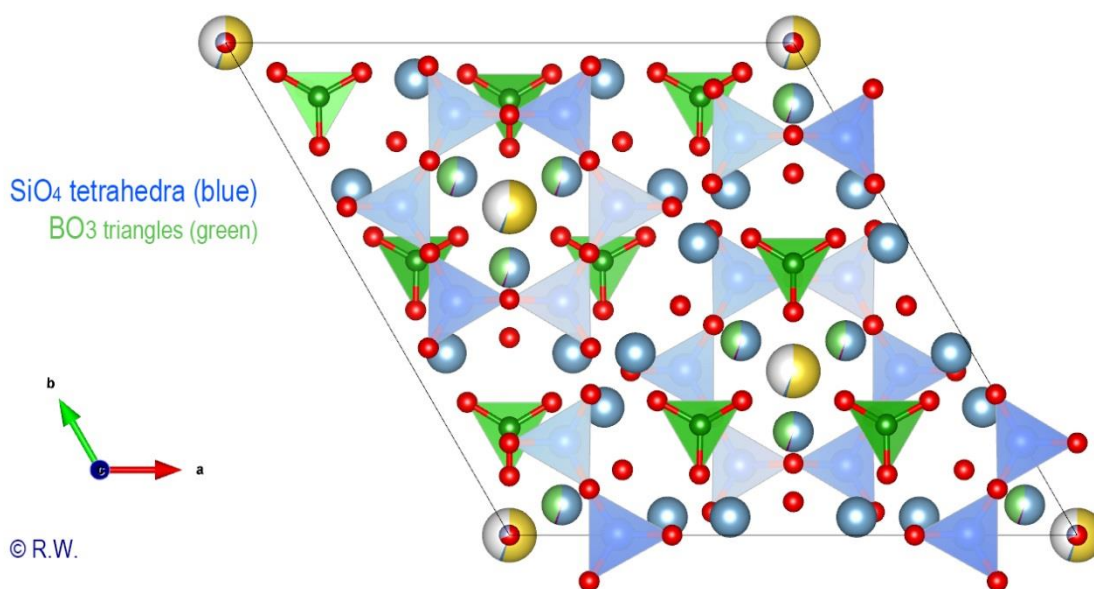


Fig. 6 – Elbaite – Crystal structure with the SiO_4 tetrahedra of coordination and planar triangles BO_3 . © R.W.

Elbaite is highly piezoelectric and pyroelectric. These last properties are typical of minerals that do not have a symmetry Center, which means that no face has any other parallel face. The pinacoid (crystallographic form with 2 parallel faces) does not exist in this case and it is replaced by the **pedion** (crystalline form characterized by a single face). So, the two basal ends of the prism are different to the point of bearing different names, the **analogous pole** (the upper pole - whose electric potential is of the same sign as the temperature change) and the **antilogous pole** (which potential varies as the opposite of the temperature change). This behavior is called **pyroelectricity**. In the figure (Fig. 6) we can see the triangular bases of $[\text{SiO}_4]$ tetrahedra are all oriented in the same direction. An angled view shows the profile of the unit cell (Fig. 7).

Piezoelectricity is the phenomenon of appearance of electrical charges at the poles of a tourmaline crystal when it is subjected to pressure and vice versa. The application of an electrical voltage at the ends of the crystal induces a change in its dimensions (a feature widely used for quartz that also does not have a center of symmetry). The tourmaline of Madagascar was used for the manufacture of the sonars used during the First World War.

In profile view, the cell reveals its secrets. Above and at the center of the cyclosilicate ring, a more bulky cation is seen, that is sodium the Na^+ ion in the case of elbaite. The three triangular $(\text{BO}_3)^{3-}$ anions which are better seen in the

previous figure (Fig. 6), are located at the lower end of the $[\text{SiO}_4]$ tetrahedra. Na atoms are located at the X sites. The X spheres of the general sketch (Fig. 7) are two-colored, because the X sites can be occupied by Na or Ca or can be left vacant, depending on the tourmaline species.

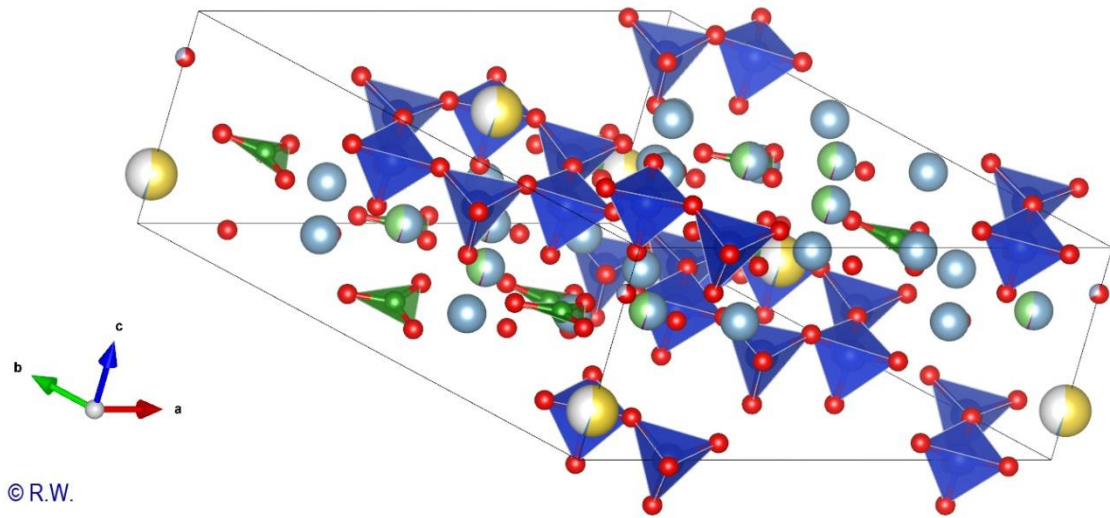
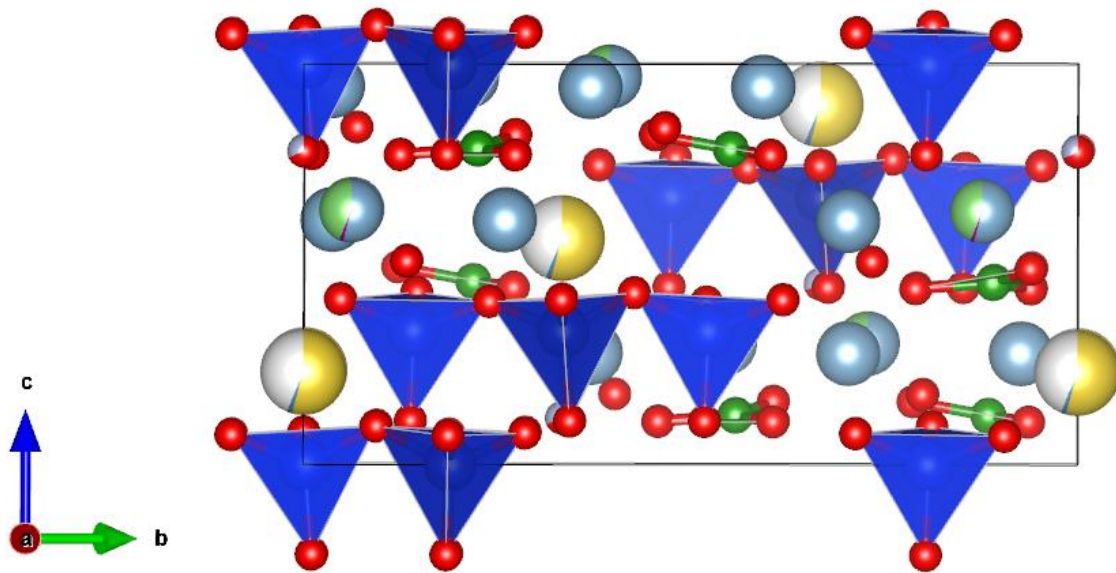


Fig. 7 – Pivoting the unit cell of elbaite. © R.W.



Elbaite - «c» axis : elongation of crystal
Unit cell profile

Fig. 8 – Unit cell profile of elbaite with in blue the tetrahedra $[\text{SiO}_4]$, bore atom (green), sodium (yellow) and aluminum (light blue). © R.W.

The following figure (Fig. 8) is much more explicit because it shows in profile the contents of this unit cell. The $[\text{SiO}_4]$ (blue) tetrahedra, **all oriented** in the same direction, namely the tip directed towards the (lower) antilogue pole, are easily noticeable. It is this feature of the structure that prohibits the presence of a Symmetry Center. We also see that the borate anions are not rigorously coplanar with cyclosilicates rings, because of the deformations induced by bulky X cations. The oxygen atoms are stratified and they participate in the coordination bonds of all the atoms of this complex building. The Al^{3+} cations occupy the other spaces of this trigonal structure (Fig. 8).

Coordinating polyhedra

Na-O₉ Polyhedron: Each anionic group $[(\text{BO}_3)_3 (\text{Si}_6\text{O}_{18})]$ is attached to an X cation (in yellow, Fig. 8) located slightly above it. It is the bulky Na^+ cation which is located on this X-O₉ site, a coordination polyhedron with 9 ligands. In short, it is centered above the cyclosilicate anion.

Al-O₆ octahedra: The 9 elbaite octahedral sites Y and Z are occupied by aluminum atoms (Fig. 9). Like a double pyramid, an octahedron is a site of coordination with 6 bonds. A quick look at the general formula shows that two possible situations exist for Al^{3+} , either the Z or Y sites. The figure (Fig. 10) highlights the location of the 3 Y sites, while the other (Fig. 11) shows the 6 Z sites.

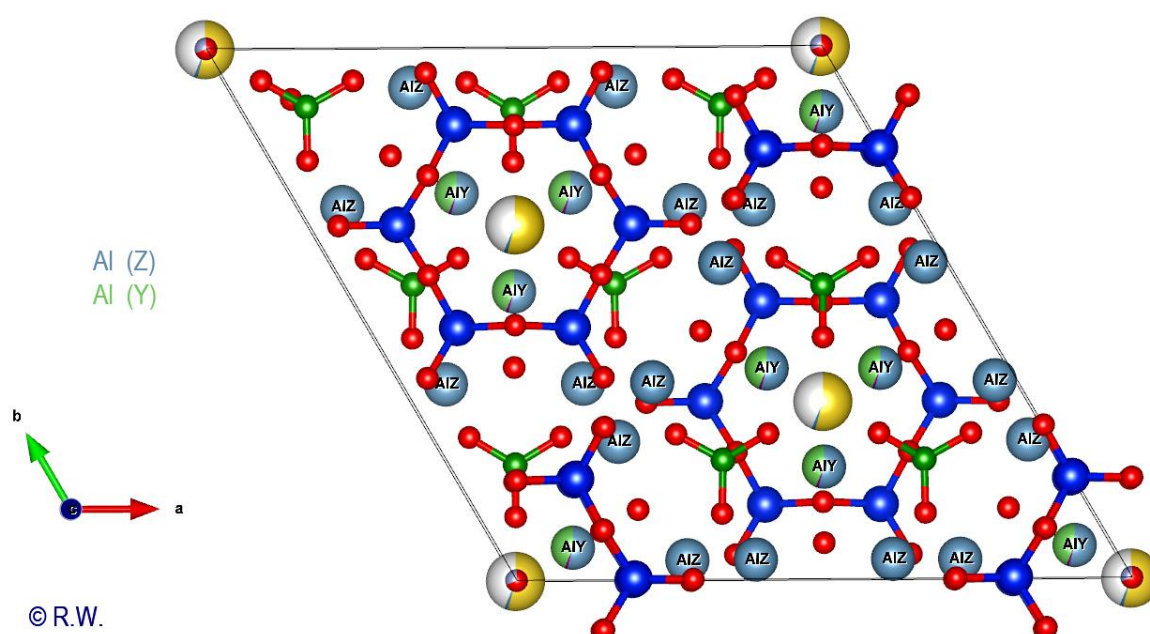


Fig. 9 – Elbaite - Polyhedral yellow sites $X = \text{Na}^+$
Octahedral slightly blue sites $Y, Z = \text{Al}^{3+}$ © R.W.

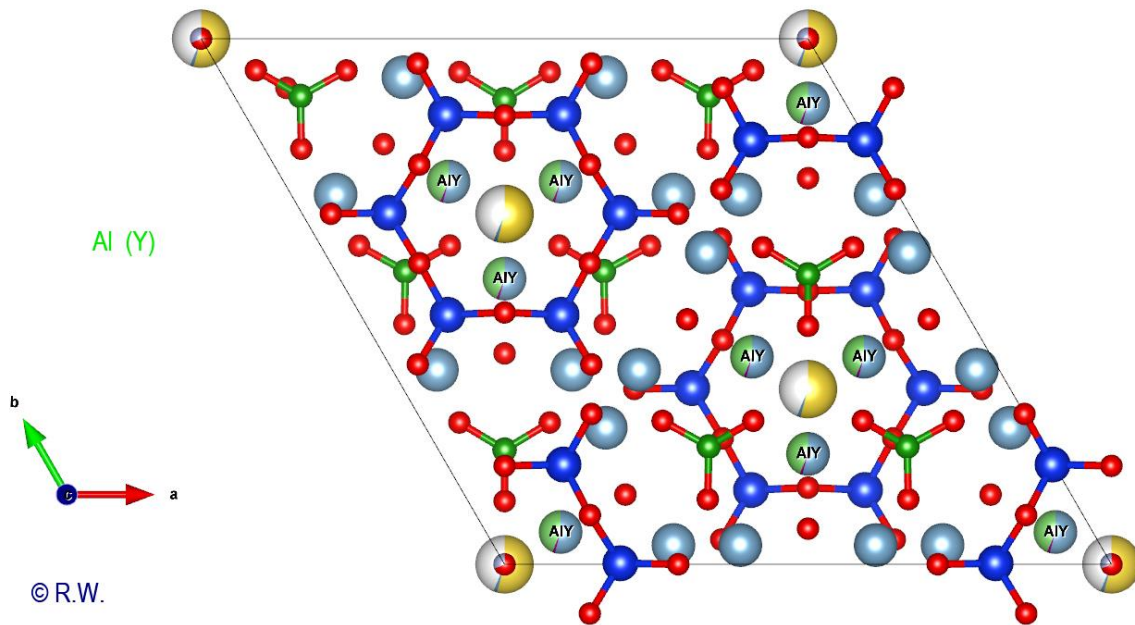


Fig. 10 – Elbaite – Octahedral sites Y (slightly blue, annotated Y) : Al^{3+} © R.W.

These considerations correspond to an ideal case (elbaite), because many cationic substitutions (and even vacant sites symbolized by the sign $\square$) can take place giving this multiplicity of different species of tourmaline. Some are more or less compatible with each other, others absolutely not. These are the domains of partial "solid solutions".

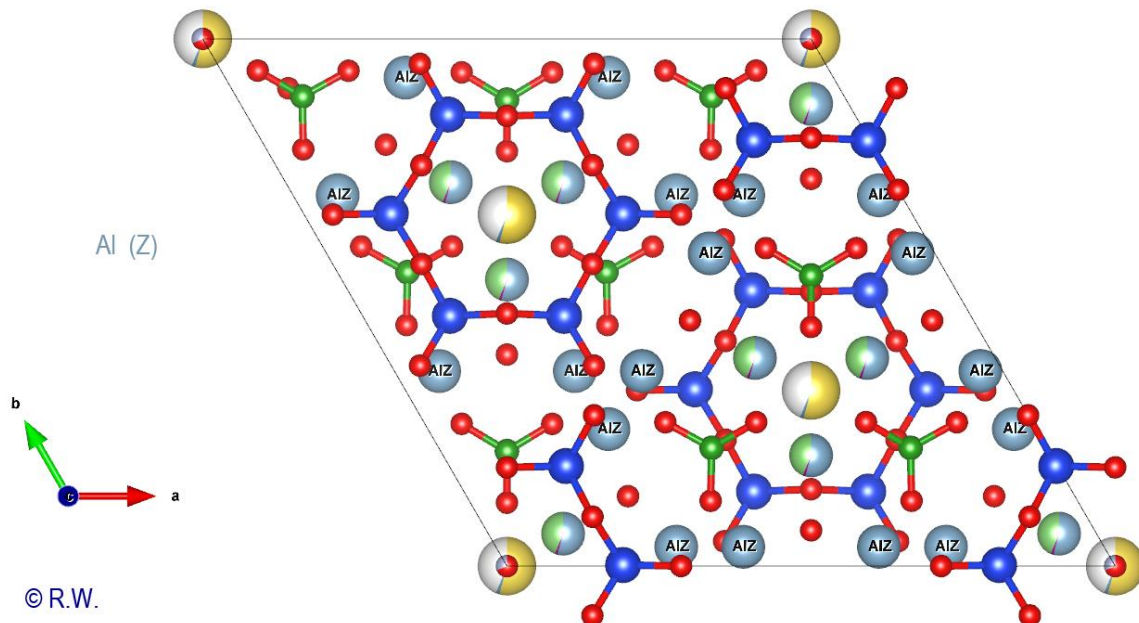


Fig. 11 – Elbaite – Al^{3+} in octahedral sites Z. © R.W.

These observations demonstrate that in each of its details, trigonal symmetry is obeyed. One may better understand that the main habitus of a crystal, as well as the appearance of facets modifying it, are closely correlated to the intimate structure of the building. The hexagonal cyclosilicate anion is surmounted by the bulky cation Na^+ . It is surrounded by 3 Al^{3+} in Y sites whereas 6 Al^{3+} (Z) encircle the cyclosilicate anion (Fig. 11).

The introduction of coordination polyhedra does not simplify the drawing (Fig. 12). But seen in profile, this purged drawing of $[\text{SiO}_4]$ tetrahedra illustrates the presence of the Al^{3+} cations packaged in the spaces left by the anions. The whole structure of elbaite is proposed in the figure (Fig. 13), with the Na polyhedra well displayed.

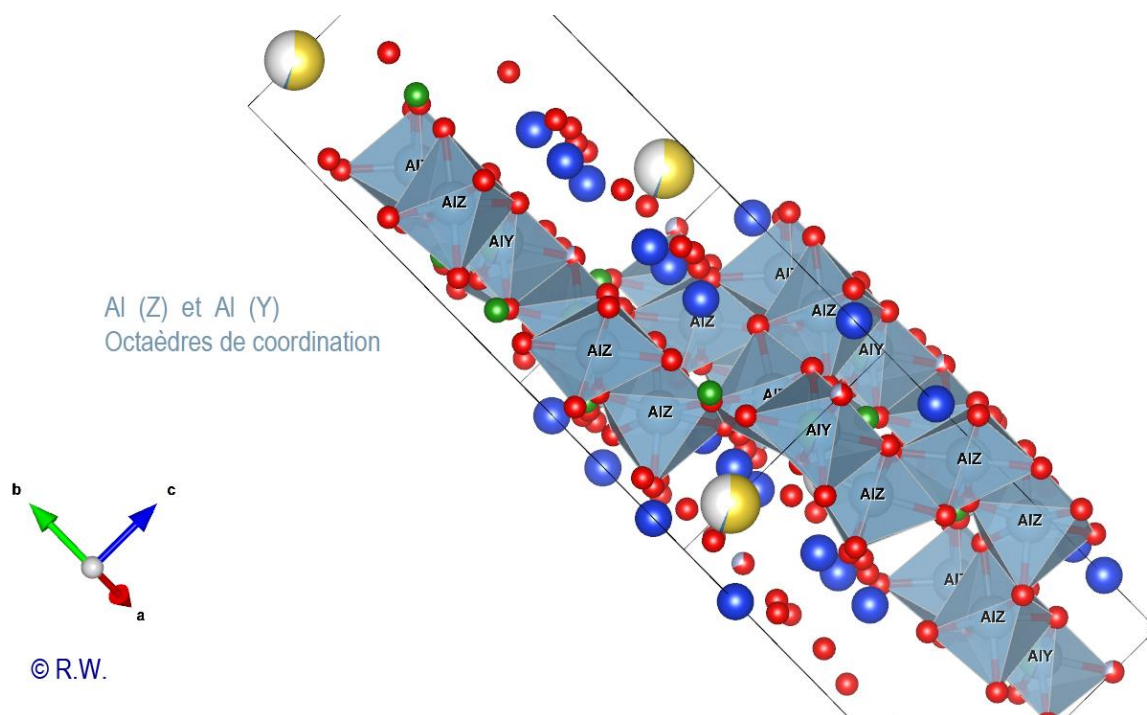


Fig. 12 – Profile view of the cationic package Al^{3+} © R.W.

CONCLUSION

The classification of the various tourmalines is a tedious task that the reader will approach on a case by case basis. The main constant is the anionic component. These are borosilicates. *After much hesitation*, the mystery surrounding tourmaline prompted us to develop and present this structural aspect, often touched but never presented, in the bulletin of the Belgian club AGAB-minibul (2017, vol.50, 4, p.85-97). The main difficulty lies in the reading

of the spatial arrangement of the various atoms and groups of atoms in the crystallographic drawings.

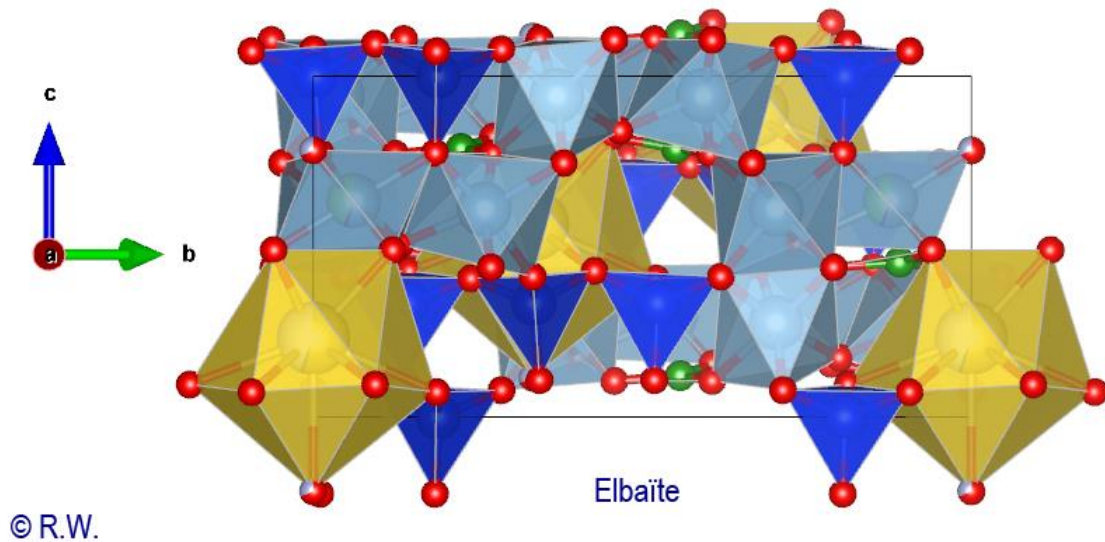


Fig. 13 – Elbaite, profile view structure, with polyhedra $[NaO_9]$ © R.W.

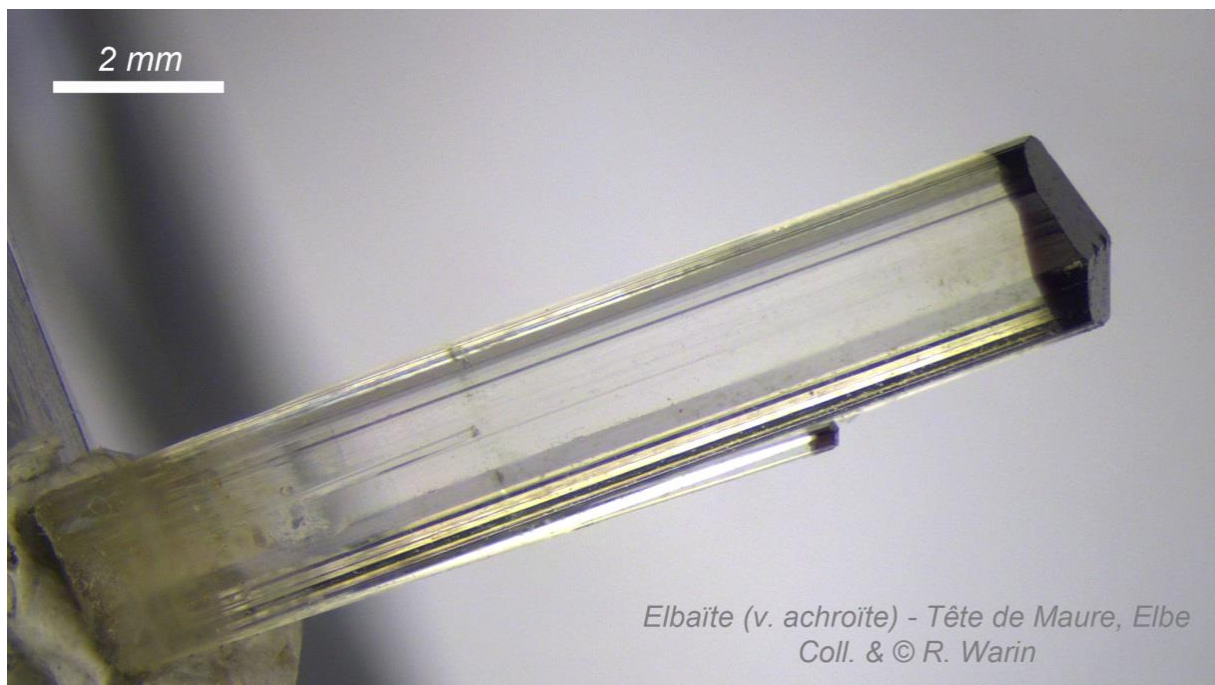


Fig. 14 – Elbaite (v. achroite) “Moor’s head », Elba (It.) – Coll. & © R.W.

Elbaite of the type locality (Elba Island, Tuscany, Italy) has its origin in sodolithium pegmatites which makes it much rarer than black schorlites ($Y = Fe^{2+}$). In the Island of Elba it can take soft pastel colors or even be colorless (achroite variety) with often a black top, called "Moor's head" (Fig 14).

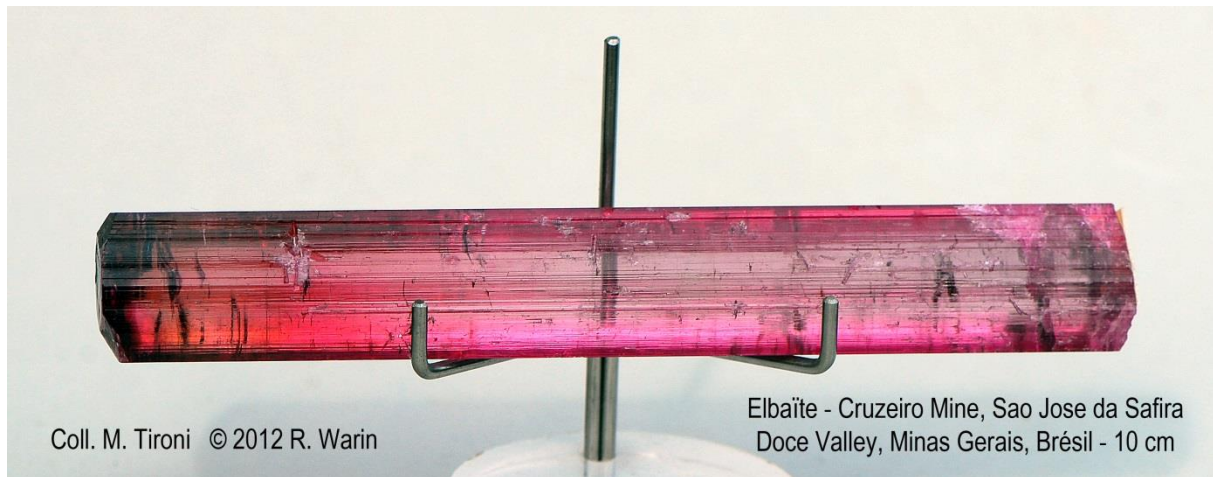


Fig. 15 –Elbaite – Cruzeiro Mine, Sao Jose da Safira, Doce Valley, Minas Gerais, Brazil (10 cm). Coll. M. Tironi – Ste Marie 2012 © R. Warin.

Postface



Fig. 16 – Liddicoatite-(F) (Madagascar), one of the many species of tourmaline. Perpendicular section to the vertical axis. The ternary symmetry is obvious. Munich 2016 © R. Warin.

Reading such an article is difficult and it will often be superficial. It assumes "prerequisites" notions, but it appeared to me that certain facts could be underlined to show the origin of the losses of symmetry of the crystal and the appearance of mysterious and yet useful properties such as pyroelectricity and piezoelectricity. In another well-known example of applied piezoelectricity, quartz watches use the resonance of a quartz tuning fork to create regular pulses. This resonator plays the role of the old balance wheels. This property is at the base of the synthesis of many artificial compounds such as ceramics or piezoelectric polymers. The industrial development of these techniques is limitless. With quartz, tourmaline has allowed the discovery of such phenomena. The first demonstration of the direct quartz piezoelectric effect is due to Pierre and Jacques Curie in 1880.

Many thanks to Jordi Fabre who several times suggested me to present an English version of this topic on the FMF forum.

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