

## NOVEL USE OF BOROSILICATES IN GEOTHERMOBAROMETRY

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### Background of the project

Terrestrial planets (like Venus, Earth, Mars) are planets, which are composed preliminary of silicates or metals. All terrestrial planets may have the same basic type of structure; such as a metallic core (mostly iron), with a surrounding silicate mantle. More than 90 % of the Earth's crust is composed of silicates. Although the element boron is rare in the Universe and solar system due to trace formation in the Big Bang and in stars, is a quintessential element of the Earth's upper continental crust. Processes that created the continental crust also enriched it in boron, and, as a result, a great diversity of boron minerals are among the most accessible of useful compounds to humankind (GREW, 2015). Boron is also needed by life. Some scientists suggested that boron was necessary to catalyze the production of RNA on Mars, with life transported to Earth via a meteorite about 3 billion years ago (NEVEU et al., 2013). Boron is a widely occurring element in minerals found in the Earth's crust. It is an essential constituent of a number of silicates, forming the complex borosilicates, some of which are rather common minerals, like members of the tourmaline and dumortierite supergroup.

### Borosilicates and their relationship to the formation conditions

Although many articles about minerals from the tourmaline and dumortierite supergroup have been published in the past, detailed investigations of the relation between crystal chemistry and pressure-temperature conditions are still missing. A systematic investigation of natural borosilicates from different geological environments, which are petrologically well characterized, as well as synthetic borosilicates, which are synthesized under precisely defined pressure-temperature conditions, can lead to information about important relationships.

Although many scientists see great potential for using of borosilicates in geothermobarometry, many questions have not yet been solved. Especially the intersite order-disorder of Mg, Fe and Al into the crystallographic positions and the occupants B and Al at the tetrahedral sites can lead to interesting correlations

to pressure-temperature conditions. Studies are also being conducted to establish correlations between different crystallographic site on samples of different origins. This is also a completely new idea, but it could be that such linear functions plot in different fields and that the slope is dependent on the temperature during tourmaline crystallisation. Although tetrahedrally-coordinated B is known to occur in tourmalines and dumortierites synthesized at high pressures, it is not clear how exactly B and Al at the tetrahedral sites are related to the pressure-temperature conditions as well as to the fluid and bulk composition of the rock composition. To get more information about structural features of the most common borosilicates of the Earth's crust it was planned to synthesize such phases at (U)HP conditions. In addition, natural borosilicates originating from different geotectonic environments and partly from (U)HP rocks should be investigated. This study was designed to expand our knowledge of the effects of site partitioning and interactions in borosilicates. The strategic research of this FWF project includes many new ideas and will be particularly helpful for the future use of borosilicates in geothermobarometry, but also for the production of synthetic tourmaline for technical applications.

### New insights

First, a tourmaline from the tourmaline-containing quartzite of the Central African fold belt was examined. The Mg-rich tourmaline (dravite) is embedded in a kaolin-poor quartzite, which, in addition to quartz and tourmaline, also consists of biotite and muscovite. The structure and chemistry of Fe-containing dravite shows only a small vacancy at the *X* site, which suggests that the tourmaline crystallizes at a high temperature >750 °C (GANWA et al., 2022). This is in agreement with previous work which shows that the metamorphic peak in the associated biotite gneiss reaches 825 °C.

During the 43<sup>rd</sup> New Mexico Mineral Symposium (Socorro, New Mexico, USA) an invited talk was given on tourmalines from Erzgebirge, Germany (ERTL, 2023a). New data on schorl and fluor-schorl from the type localities as well as on oxy-schorl from diamond-bearing rocks were provided. A talk on F and Li enrichment in late-stage fluids of a tourmaline-bearing LCT pegmatite from Fonte del Prete, San Piero in Campo, Elba Island, Italy, was presented at the University of Milan during EMPG 2023 (ERTL et al., 2023).

Subsequently, the problem of vacancies at the [6]-coordinated sites in minerals of the tourmaline group was addressed (ERTL, 2023b). Tourmaline has two different [6]-coordinated sites, the *Y* site and the *Z* site. Vacancies were reported from both sites. Based on high-quality chemical and single-crystal structural data, increasing fractions of specific short-range order configurations are usually required to generate *Y*-site vacancies. Therefore, tourmalines enriched in cations with charge 2+ (Fe<sup>2+</sup>, Mn<sup>2+</sup>, Mg) contain only insignificant *Y*-site vacancies. Only Al<sup>3+</sup>-rich tourmalines may have significant vacancies at the *Y* site. A new calculation procedure for the Li content was proposed for tourmaline samples when no chemical data for Li is available. Tourmalines that are either Fe<sup>2+</sup>-rich or belong to the Schorl-Dravite series do not appear to contain significant *Y*-site vacancies. It was found that the *Z* site has only insignificant vacancies (ERTL, 2023b).

During the CSCM 2024 conference a first attempt to use correlations in tourmaline as a thermometer was presented (ERTL, 2024). Linear functions between the occupancy of different crystallographic tourmaline sites usually exhibit different slopes when recording samples from different localities. To develop a thermometer, tourmalines synthesized at 650 °C / 150 MPa and at 750 °C / 200 MPa were used for calibration. The resulting formula with minerals of the tourmaline group could have the potential to be used as a geothermometer (ERTL, 2024). The first results seem promising, however, problems of Al-Mg disorder between the two [6]-coordinated sites need to be addressed.

Preliminary investigations on a tourmaline associated with garnet from a pegmatoid of the Bohemian Massif, Austria, led to a detailed publication on a sector-zoned garnet (KOHN et al., 2024). Almandine-spessartine garnet from the Moldanubian Zone exhibits distinctive crystal growth features that were formed during the transition from the pegmatoid magmatic to the subsolidus state. Directional garnet growth leads to asymmetric zoning. The contribution of submicron and nano-inclusions of different phases is crucial for thermobarometric methods (KOHN et al., 2024).

A new B- and Al-rich tourmaline with formula  $\text{NaAl}_3\text{Al}_6(\text{Si}_4\text{B}_2\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$ , a late stage product of an open pocket from a highly fractionated granitic pegmatite in Madagascar, was named ertlite after the project leader (CEMPÍREK et al., 2024). It was already suggested by ERTL (2018) that very  $^{14}\text{B}$ -rich tourmalines are most likely to occur in low-temperature environments, such as in highly developed pegmatitic rocks, and that such B-rich tourmalines could occur there as late-stage products. Ten years earlier a hypothetical B-rich tourmaline end-member with exactly the same formula as ertlite was proposed by ERTL et al. (2008). It is great that predictions sometimes come true. In the final description of the tourmaline ertlite (CEMPÍREK et al., 2025), another occurrence of this tourmaline was also mentioned. The occurrence of this sample is located in Myanmar and its chemical composition is very close to the end-member formula. In the meantime, a third location of ertlite has been verified, located in the Koralpe, Styria (BAČÍK & ERTL, 2025).

Aluminum-rich tourmaline can contain significant amounts of lithium. Until now, syntheses have not been successful in producing Li-rich tourmalines. Because it is still not clear how  $^7\text{Li}$  enters the tourmaline structure, possible short-range orders, including Li, are discussed using bond valence calculations (BAČÍK & ERTL, 2025). Structural arrangement graphs of the Y-site neighbourhood in the structure of elbaitic tourmalines were investigated to determine more information about their stability and possible short-range ordering. Investigations by BAČÍK & ERTL (2025) have shown that tourmaline with varying amounts of Na but no Ca can only contain  $\leq 1$  apfu (atoms per formula unit)  $^7\text{Li}$ . This is consistent with the composition of synthetic tourmalines. Tourmaline with higher Li content ( $\text{Li} > 1$  apfu) can form when Ca is included. Such tourmaline requires fluorine because more Li results in O1 underbonding, whereas more  $^7\text{Al}$  leads to O1 overbonding. Underbonding of O1 is preferable for F because OH at the O1 site usually has a bond valence sum higher than 1.00 vu (BAČÍK & ERTL, 2025). This explains why

liddicoatitic tourmaline is enriched in F. If no F is present in the starting material of a tourmaline synthesis, significant amounts of cations such as B and Al are incorporated into the tetrahedral position. Ultimately, only a smaller proportion of Li can be incorporated. In order to synthesize Li-rich tourmalines, BACÍK & ERTL (2025) recommend that the starting material also contains both Ca and F.

A preliminary study by PEZZOTTA et al. (2025) provided new evidence that Li-bearing pegmatitic tourmaline crystallized from the Rosina pegmatite on Elba Island, Italy, in two events. In an earlier investigation ALTIERI et al. (2023) proposed a genetic model in which, as a consequence of a pocket rupture event, chemical alteration of Fe- and Mn-rich minerals that formed early in the pegmatitic rock surrounding the cavities occurred through leaching processes, produced by the action of the highly reactive late-stage cavity fluids. Such processes could be responsible for the release of Fe and Mn in the geochemical system, allowing the formation of the latestage dark-colored terminations in the tourmaline crystals (ALTIERI et al., 2023). A later study by PEZZOTTA et al. (2025) was carried out using tourmaline crystals from pockets of this pegmatite. When the F content is plotted against the X-site charge of two tourmaline crystals, it can be seen that all zones, except the termination, show a positive correlation with  $r^2 \approx 1.00$ . In both cases the termination lies outside of this linear function. This observation was interpreted as an evidence that the terminations of the tourmaline crystals in the Rosina pegmatite grew during a different event than the previously grown zones (PEZZOTTA et al., 2025).

A tourmaline with probably the highest possible amount of tetrahedrally coordinated B and the approximate formula  $\text{NaAl}_3\text{Al}_6(\text{Si}_3\text{B}_3\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3(\text{OH})$ , synthesized from a reaction mixture of  $0.625 \text{ Na}_2\text{O} \cdot 4.5 \text{ Al}_2\text{O}_3 \cdot 6 \text{ SiO}_2 \cdot 3 \text{ B}_2\text{O}_3 + \text{excess H}_2\text{O}$  at  $400^\circ\text{C} / 1500 \text{ MPa}$ , was structurally and chemically analysed (ERTL et al., 2025). Structural parameters obtained from XRD patterns analysed by Rietveld refinement are  $a = 15.562(3)$ ,  $c = 7.001(1) \text{ \AA}$ . An extrapolation by ERTL (2018) for a B-rich tourmaline with the same formula resulted in very similar lattice parameters of  $a = 15.5$ ,  $c = 7.0 \text{ \AA}$ . The resulting formula (B and H were calculated) of this synthetic tourmaline was given by ERTL et al. (2025) as  $(\text{Na}_{0.97}\text{Ca}_{0.02}\square_{0.01})\text{Al}_{3.00}\text{Al}_{6.00}(\text{Si}_{3.17}\text{B}_{2.83}\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3[(\text{OH})_{0.82}\text{O}_{0.18}]$ . The T-site occupancy is in very good agreement with the result of the Rietveld refinement with  $[\text{Si}_{3.12}\text{B}_{2.88(12)}]$ . Based on temperature-dependent correlations, it was concluded that the formation of such tourmaline in hydrothermal to low pressure environments is unlikely, since the expected temperature would be  $<150^\circ\text{C}$ .

## Outlook

The project is currently in its final year, and the focus now is on collecting and processing the numerous scientific insights. It seems that I am very close to developing a geothermometer based on tourmaline, which allows good temperature estimates of the respective rock. Such a discovery would also be important for geology, petrology and materials science. One impact could be the discovery of additional raw materials such as rare earth minerals in certain rocks.

Tourmaline is a natural resource known for its stability and robustness, making it suitable for use in sensors. Tourmaline can offer volumetric sensitivity, meaning it responds to pressure changes throughout the entire volume of the crystal, not just surface contact. Tourmaline-based sensors can be integrated into printed circuit boards (PCBs) to enable a variety of applications, such as pressure measurements in industrial processes, automotive engineering, or medical technology. However, synthetic tourmaline for technical use have not yet been successfully produced. My research has already uncovered interesting connections; a better understanding of the conditions under which tourmaline is formed would be the first step towards successfully production of tourmaline for technical use.

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