Research proposal – PhD in Earth Sciences

XXXIX cycle

A.Y. 2023-2024

Study of color mechanisms in natural and treated gemstone tourmalines, with definition of a scientific protocol

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Introduction and state of the art

Tourmalines are a supergroup of chemically complex borosilicate minerals [1].

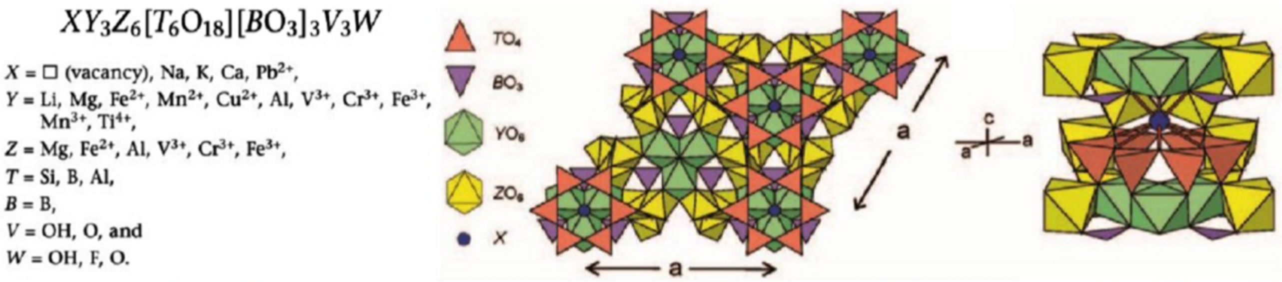

Fig. 1 General formula and schematic representation of the crystalline structure of tourmaline with the list of the main cations and anions that can occupy the various sites. From Hawthorne & Dirlam (2011).

Many studies have shown that transition element cations present in the Y and Z sites influence the wide color spectrum of tourmaline, including black and the colorless variety. The causes of the color origin in tourmalines require detailed studies, due to the presence of multiple processes that interact with each other [2,3]. For example, the pinkish-red can be obtained from the Mn^{3+} or the Mn^{2+}- F bond; yellow gives (Mn^{2+}+ Ti^{4+}); green from Fe^{2+}, (Fe^{2+}+Ti^{4+}), Cr^{3+} or V^{3+}; Blue from Fe^{2+} or Cu^{2+}.

The complicated mechanisms responsible for the chromatic diversity that confers gemological value on tourmaline are mostly described by the absorption spectrum and crystal field theory. [4,5]. The type of ion, defects and distortion of the polyhedra can lead to specific electronic transitions that could affect the color [2]. Therefore, the divergent and incomplete opinions on the causes and mechanism of natural and laboratory-treated color does not allow us to define a univocal model.

For this purpose, chemical, structural and spectroscopic analyses will be used to characterized samples of gemological interest , in particular the paraíba and rubellite varieties, both natural and treated thermally and by irradiation.

The Paraíba tourmaline, in particular, with its vivid colors from turquoise to neon blue to blue-green, is now one of the most expensive gems on the market, with values that can exceed 50,000 USD/carat. The bright blue specimens owe their characteristic color to Cu^{2+}, present in concentrations of hundreds of ppm by weight [7], while Fe is less than 1% by weight and Mg is low [10].

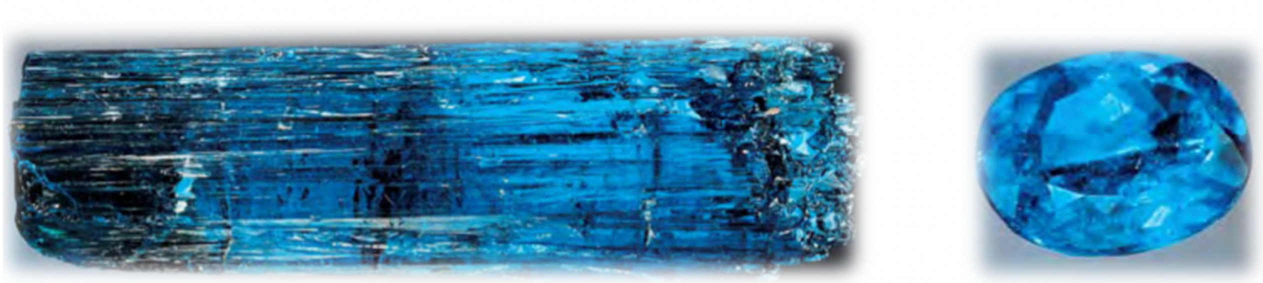

Fig. 2 Paraíba copper tourmaline, raw and cut crystal. Mike Scott Collection; photo by Harold & Erica Van Pelt.

The largest and most recent alluvial deposit known in the world of cupriferous tourmalines with colors similar to Paraíba is the Mavuco area (Alto Ligonha, Mozambique) [11]. The samples available for this study come from these residual alluvial deposits where hundreds of kilograms of gem-quality raw tourmaline are retrieved; nevertheless, only 10% of the samples display colors that can be classified as paraíba. [10]. Detailed chemical and spectroscopic studies on these rare materials would allow us to increase knowledge on the subject, understanding the actual presence of paraíba in Mozambique and the differences between treated and natural.

Fig. 3 a) Accumulation horizon of the residual material, where the tourmaline roughs are extracted.
b.c) Rough cupriferous tourmaline with different hues. Photo Dr. Federico Pezzotta.

Red hues rubellite is a very popular gemstone on the current market. As result, pale pink or colorless crystals are treated with irradiation in the laboratory to produce a more intense red color [4], while thermal treatment acts in the opposite direction, reducing the color saturation [6]. Both techniques seem to involve a passage of Mn from +2 to +3, the presence of "color centers" or Fe^{3+} [7,8,9]. Detailed studies are therefore required to understand the causes and mechanisms of the red color of rubellite and the laboratory conditions to obtain such colors.

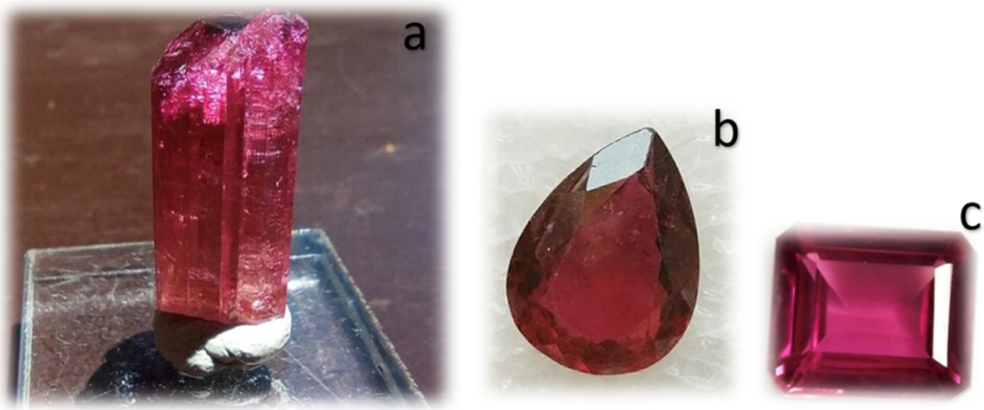

Fig. 4 a) Rough rubellite red tourmaline crystal; **b)** Cut natural rubellite red tourmaline;
c) Cut rubellite red tourmaline treated by irradiation. Riccardo Luppi Collection; photo Riccardo Luppi.

The multi-analytical approach (EMP = Electron MicroProbe, FTIR = Fourier Transform InfraRed spectroscopy, Raman = Raman spectroscopy, OAS = Optical Absorption Spectroscopy, SREF = Structural REFinement, LIBS = Laser Induced Breakdown Spectroscopy) of this project combines traditional techniques and advanced methods to investigate the chemical-physical variables that lead to color change, following natural and laboratory processes. The use of scientific gemology, a link between the knowledge of the academic world and the practical experience of the commercial sector, would allow the definition of a treatment protocol. This set of procedures would analytically describe what coloring results are obtained for a specific chemical composition after certain treatment conditions. The results of this study is fundamental for gemological certification laboratories. They will allow the identification of natural materials and defend the market from counterfeiting. The results are expected to be submitted to the LMHC (Laboratory Manual Harmonized Committee), which brings together the best gemological laboratories in Europe, United States and Asia with the main objective of correct nomenclature, dissemination and harmonization of the language used in gemological reports.

Research objectives

General Objective:

• Understanding of the color mechanisms in gemstone tourmalines, with the development of a scientifically acceptable treatment protocol and correct distinction between natural and laboratory-treated.

Specific objectives:

• Chemical-physical, spectroscopic and structural characterization of natural and treated (heating and irradiation) gem-quality tourmaline samples.

• Crystal-chemical model for the causes of origin and mechanisms of color in natural and treated tourmaline.

• Understanding of the chemical-physical aspects responsible for the "neon" variety of tourmaline color and development of an evaluation scale.

Implications and applications

The applications and implications are both in the scientific field and in the scientific gemological field applied to industry. The development of a crystal-chemical model for the interpretation of color changes would increase knowledge on the mechanisms of color in tourmalines. The development of an analytical protocol (scientific gemology) would establish a procedure on treatment conditions, allowing for the correct distinction between natural and treated and the regulation of the gem market. This would offer a valid means to the service of certification laboratories (LMHC).The development of this knowledge at the service of gemological certification laboratories could strongly contribute to promoting a consumer protection device in Italy, a need that is very felt, which has produced seven passages between the Chambers with various Bills, the most recent in 2017.

Work plan

The planned research activities will be carried out on valuable and rare samples of gem-quality tourmaline, coming from Mozambique, Madagascar, Elba Island, Pakistan and Afghanistan supplied by some companies in the gem mining sector and also coming from public museum collections, through Federico Pezzotta (Natural History Museum of Milan).
In this project, the direct contact with the extractive source testifies to the strong link between the theoretical scientific part and the application part of the extractive work. Access to valuable materials, which are difficult to find and therefore still little studied, guarantees the feasibility of the project and excellent prospects.

Analysis and treatments on samples

Samples of Paraíba tourmaline and other cupriferous color varieties, coming directly from the extraction mine (Mavuco, Mozambique), will be classified into different color categories based on the natural color observed on the **c** and **a** axis of each sample. Subsequently, all the samples will be subjected to heat treatment in oxidizing and/or reducing conditions, irradiation with electrons (selected samples) and consequent classification of the color obtained in the various steps of the treatment processes. Chemical, structural and spectroscopic analyses will be carried out on the most significant and representative samples of the main color categories.
These studies and treatments, including partly unpublished experiments, such as heating in a reducing environment and irradiation, will allow us to understand the mechanisms, causes and genesis of color zoning as well as the "neon" effect. Studies and treatments on which the undersigned has already begun to develop specific application skills at the Mozambique Mining laboratories at M.C.P Srl (Milan). The results will

contribute to the development of scientifically tested procedures aimed at developing a methodical treatment protocol that includes both heating and irradiation.

Starting from the research carried out during my master's thesis, studies will be carried out on samples of acroite (colorless tourmaline) from the Island of Elba and Stak-Nala (Pakistan). Rubellite samples from Ampatsikahitra and Anjanabonoina (Madagascar) and from Afghan localities will be treated (heating and irradiation) and analyzed chemically, structurally and spectroscopically to better understand the influence of the treatments on the red color of the tourmalines. Currently, in fact, it is not possible to discriminate "natural" red from "treated" red using the gemological techniques. The heating treatments in a controlled atmosphere in reducing and oxidizing environments will be carried out at the Swedish Museum of Natural History in Stockholm and the headquarters of the Mineralogical Collection Professionals - M.C.P Srl in Milan. The treatments by irradiation with electrons will be carried out at the ENEA Research Center in Frascati. The structural analysis, single crystal X-ray diffraction and chemical analyzes with EMPA at the Sapienza University of Rome and the spectroscopic analyzes (FTIR, OAS, Raman and LIBS) will be performed at the Swedish Museum of Natural History in Stockholm and the Department of Earth and Geoenvironmental Sciences of the University of Bari.

Dissemination plan

Participation in national and international conferences, workshops, and congresses in the fields of mineralogy and scientific gemology, including:

- SIMP Congress (Italian Society of Mineralogy and Petrography), 2024, 2025, 2026
- Congress and Workshop of the National Mineralogy Group, 2024, 2025, 2026
- 4th International Conference on Tourmaline, 2025, Madagascar
- 4th European Mineralogical Conference, 18-23 August 2024, Dublin
- IMA (International Mineralogical Association) Congress, 2026, China

Training activities

Attendance at this Department of seminars and courses for doctoral students and institutions such as Mineral Structure (F. Bosi) and Crystallography (P. Ballirano), Raman and FTIR Spectroscopies (L. Medeghini; A. Masi). Attendance of further seminars on mineralogy and scientific gemology at other universities (e.g. University of Milan, Pavia, Padua, Florence). As part of the project, I will have the opportunityto go to professional tourmaline treatment laboratories in Brazil and New Jersey, with the possibility of acquiring practical skills on heat treatments. Visits to the extraction sites in Mozambique are also planned, with the aim of delving into the geological, technical and production aspects.

National and International Mobility

Research activities are planned in various Italian and European institutes and laboratories. Specifically, in the first year and the first semester of the second year, compositional and structural analyzes will be performed at the Department of Earth Sciences (Sapienza University of Rome), irradiation treatments at the ENEA Research Center in Frascati and heating treatments at the Mozambique Mining, in the branch site in Milan (at M.C.P. Srl) and the Edison headquarters in New Jersey (USA). The second semester of the second year, among other things, I will carry out spectroscopic analyzes and heating treatment of samples at the Swedish Museum of Natural History, Stockholm.

Essential bibliography:

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4. Pezzotta & Laurs 2011. Elements, 7, 333–338
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8. Chaudhry & Howie 1976. Min Mag, 40, 747–751
9. Bosi & Skogby 2013. Am Miner, 98, 1442-1448
10. Okrusch et al. 2016. J Gemm, 35, 120–139
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GANTT CHART 2023-2026	1st YEAR 2023-2024				2nd YEAR 2024-2025				3rd YEAR 2025-2026			
	TRIMESTER											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
	Nov-Jan 1-3	Feb-Apr 4-6	May-Jul 7-9	Aug-Oct 10-12	Nov-Jan 13-15	Feb-Apr 16-18	May-Jul 19-21	Aug-Oct 22-24	Nov-Jan 25-27	Feb-Apr 28-30	May-Jul 31-33	Aug-Oct 34-36
Training activities	■	■	■	■	■	■	■	■	■			
Bibliographical research	■	■	■	■	■	■	■	■	■	■	■	■
Research activities	A1- A2	A2	A2 - A3	A4 - A5	A5	A5 - A6	A7 - A8	A8 - A9	A10 - A11	A11- A12		
Milestones					T1	T2		T3		T4		
Dissemination plan				P1			P2				P3	
Mobility					■	■			■			
Meeting with supervisors	■			■		■		■		■		■
Annual report				■				■				■
Writing manuscripts					■			■			■	■
PhD Thesis											■	■

A1 = Color classification using the Munsell system of natural samples of cupriferous tourmalines from Mavuco; A2 = Heating of copper tourmalines using professional ovens in oxidizing and reducing conditions, with determination through the Munsell system of the color obtained in the various steps of the heat treatment process; A3 = Treatment by irradiation (electron accelerator) of selected samples of cupriferous tourmaline with color classification through the Munsell system; A4 = Chemical characterization with electron microprobe (EMP) of thin sections of cupriferous tourmaline samples; A5 = IR, optical absorption (UV/VIS/NIR), Raman and LIBS spectroscopic analyzes of specific natural and treated (heating and irradiation) copper tourmaline samples, representative of the main color categories; A6 = Structural analyzes by single crystal X-ray diffraction, for the most significant samples; A7 = Color classification through Munsell system and sawing into two sections of rubellite samples from Madagascar and Afghanistan; A8 = Heating of the samples (one of the two halves) of rubellite tourmaline from Madagascar and Afghanistan through professional and controlled atmosphere ovens until colorless samples are obtained; A9 = Sawing of the colorless samples into two halves and irradiation (electron accelerator) of one of the two sections to restore the samples to a rubellite red color with classification of the exact color through the Munsell system; A10 = Chemical characterization with electron microprobe (EMP) of thin sections of rubellite samples from Madagascar and Afghanistan; A11 = IR, optical absorption (UV/VIS/NIR), Raman and LIBS spectroscopic analyzes of samples from Madagascar, Afghanistan, Pakistan and Elba Island, natural and treated by heating and irradiation; A12 = Structural analyzes by single crystal X-ray diffraction, for the most significant samples.

T1 = In-depth characterization of the "neon" color in tourmalines and development of a rating scale; T2 = Understanding the causes of the origin of color in Paraíba tourmalines. Distinction and valorization of natural paraiba from treated ones; T3 = Development of the protocol on the treatment conditions of tourmalines; T4 = Understanding color mechanisms for pink-red tourmalines. Recognition and distinction of natural and treated red tourmaline.

P1 = *4th European Mineralogical Conference (EMC)*; P2 = *4th International Conference on Tourmaline* (*TUR2025);* P3 = IMA (International Mineralogical Association) Congress.