Definition of a genetic model for the dark-colored overgrowths in pegmatitic gem tourmaline crystals

Alessandra Altieri

Dipartimento di Scienze della Terra, Università di Roma La Sapienza, Piazzale Aldo Moro 5, 00185, Roma, Italia

RESEARCH'S INTRODUCTION AND AIM

Pegmatitic gem tourmaline crystals commonly display a sharp transition to dark color at the analogous termination; one of the best example is the so-called "Moor's head" textural type, which characterize the tourmaline crystals from Elba Island (Pezzotta, 2021). Such terminations show a wide range of morphological characteristics: they may occur as a narrow overgrowth with a sharp and lustrous pedion face terminating the crystal or as a thick overgrowth with rough pyramidal faces characterized by a fibrous texture that, occasionally, can be composed of an aggregate of long parallel needles (Fig. 1). However, in some tourmaline crystals, the dark overgrowth can extend all over the prismatic faces, including the antilogous pole. In all these cases, such dark-coloured overgrowths can be generally described as *colour anomalies*.

The formation of color anomalies, which are typically rich in Fe and/or Mn, is related to a dramatic physico-chemical change in the geochemical system during the latest-stages of tourmaline growth. However, the true sequence of events that led to the availability of such elements in the crystallization environment, resulting in the growth of late-stage tourmalines, was still unclear.

The goal of this Ph.D research is to constrain the formation mechanisms of tourmaline dark-colored terminations. To achieve this goal, selected gem-tourmaline crystals with dark overgrowths of different colors and textural features from several miarolitic Li-bearing pegmatites located in Elba Island (Italy), were studied with a multi-analytical approach. This approach includes chemical analysis with an electron microprobe and spectroscopic investigations using Mössbauer, OAS and FTIR analyses. Results obtained, combined with structural and paragenetic information of the cavities, were used to define a genetic model for the color anomalies observed in Elba gem-tourmaline crystals. This Ph.D research was further extended to several detrital tourmaline grains collected from the secondary deposit of Mavuco (Alto Ligonha pegmatite district, NE Mozambique). Gem-quality tourmalines from the Alto Ligonha district are among the most renowned for the combination of color and rarity.

Figure 1 a) Thin black overgrowth evidenced by a lustrous pedion face at the termination of a multicolored tourmaline crystal on matrix. b) Thick black overgrowth with rough pyramidal faces at the termination of a multicolored tourmaline crystal on matrix. c) Fibrous black overgrowth on a multicolored tourmaline crystal. All specimens are from Elba Island (Italy). Private collection. A. Miglioli photo.

These features make them unique from a gemological viewpoint and therefore with a high commercial value, limiting the information regarding their crystal-chemical characteristics. To fill this gap, sixteen tourmaline grains provided by ongoing mining projects, were subjected to an in-depth analysis. Specifically, a detailed chemical characterization as well as a correlation study between compositional data and color displayed, was conducted. In addition, on selected grains with particular chromatic features, OAS analyses were performed. For all the tourmaline samples, the gemological variety was identified.

Besides their polychromatic features, most of these tourmaline grains are characterized by a dark overgrowth covering the prismatic faces. However, the genetic mechanisms responsible for these peculiar overgrowths have not been defined so far, as the pegmatitic source from which these tourmalines originated was still uncertain. This uncertainty was essentially due to the strong NYF (Niobium-Yttrium-Fluorine) geochemical affinity (Li- and B-poor composition) of the Alto Ligonha pegmatites located quite close the secondary deposit of Mavuco, as well as the rudimentary excavation techniques, which did not allow the exploration of new pegmatitic deposits in the Alto Ligonha district. To gain information about the mechanisms that led to the formation of the prismatic dark overgrowths, selected tourmaline crystals from a recently discovered pegmatitic field, the so-called "Marina" pegmatite (Mavuco area), were analyzed. The "Marina" pegmatite has been hypothesized to be the source of the detrital tourmaline grains of the Mavuco area, given its proximity to the secondary deposit and its LCT geochemical signature. Studies on tourmaline crystals from the "Marina" pegmatite were carried out to confirm the above hypothesis; specifically through the comparison of the compositional data obtained from such tourmaline crystals with those obtained from the detrital tourmalines of the Mavuco area. The same studies allowed obtain detailed information on the genesis of the dark prismatic overgrowths, which also characterize most of the detrital tourmalines.

CRYSTAL-CHEMICAL STUDY OF PEGMATITIC GEM TOURMALINE CRYSTALS FROM ELBA ISLAND (TYRRHENIAN SEA, ITALY)

Main results

Eleven tourmaline samples that represent the variety of color anomalies at the termination of Elba tourmalines were collected from different miarolitic cavities occurring in the area of San Piero and Sant'Ilario in Campo villages, within four selected pegmatitic veins distributed along the eastern border of the Monte Capanne pluton. Compositional data were collected with electron microprobe along a straight traverse parallel to the c-axis from the base to the termination of each crystal using an average

step size of 300 μm, except at the overgrowths, where the step size was reduced to about 150 μm to capture more fine-scale details. A total of 400 spot analyses were collected. Iron oxidation state was determined in selected Fe-rich overgrowths by Mössbauer spectroscopy. On the basis of the chemical data and color displayed, each sample was divided in compositionally similar zones. For each zone, atoms per formula unit (apfu) were calculated and the relative empirical formula has been determined.

It is interesting to point out that during this chemical characterization, a new mineral species of the tourmaline supergroup was discovered: celleriite, ideally $\square(Mn^{2+}_2Al)Al_6(Si_6O_{18})(BO_3)_3(OH)_3(OH)$. It was found in the Rosina pegmatite (San Piero in Campo, Elba Island, Italy) and occurs as chemically homogeneous, millimetric to
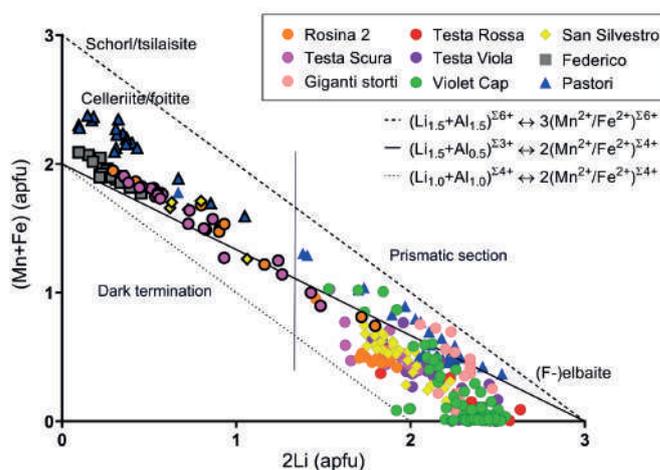

Figure 2 Plot of the content of 2Li vs. (Mn+Fe) at the Y site for each spot analysis of the tourmaline samples studied. The three lines (dashed, dotted and full) represent different degree of substitution. Symbols with black border indicate the compositions relative to the dark terminations of the different samples. For Pastori sample the Mg content was also considered. The vertical line distinguishes the compositions occurring at the crystal dark terminations (left) from those occurring in the prismatic sections (right).

sub-millimetric zones within the analogous pole of a zoned tourmaline crystal. This new mineral species was approved by the IMA-CNMNC, proposal n. 2019-089 (Bosi et al., 2022a).

In general, chemical analysis revealed that the termination of each crystal is characterized by a significant increase in Fe and/or Mn that is responsible for the color variation at the analogous pole. As expected, in the tourmaline crystals with the most significant Fe and/or Mn increase at the termination (MnO > 5 wt% and FeO > 2 wt%), the color variation is more enhanced, and the species changes from initial elbaite/fluor-elbaite, to celleriite, foitite, or schorl (Fig. 2). Such increase in Fe/Mn suggests that a dramatic chemical variation in the crystallization environment, with a new supply in Fe/Mn during the latest stages of tourmaline growth, occurred. The increase in Fe and Mn is consistent with the substitution of Li and Al at the Y site of the tourmaline structure. However, this substitution can occur in different ways ac-
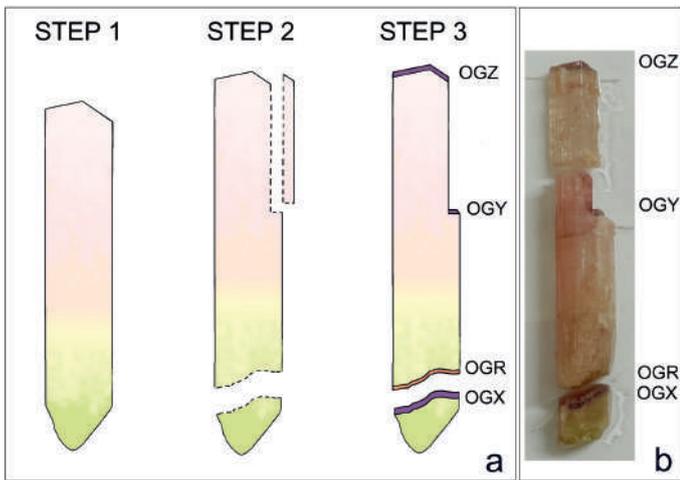
Figure 3 History of growth of the analysed tourmaline crystals. a) Schematic representation of the events that led to the collected samples. Step 1: tourmaline crystal growth from light green to pale pink in the direction of the analogous pole (c- side). Step 2: breakage of the crystal as a result of the pocket rupture event followed by changes in the chemical composition of the crystallisation environment. Step 3: generation of late-stage dark-coloured overgrowths at the analogous (OGX, OGY, OGZ) and at the antilogous (OGR) poles in a Mn-rich environment. b) Image of the tourmaline crystals analysed.
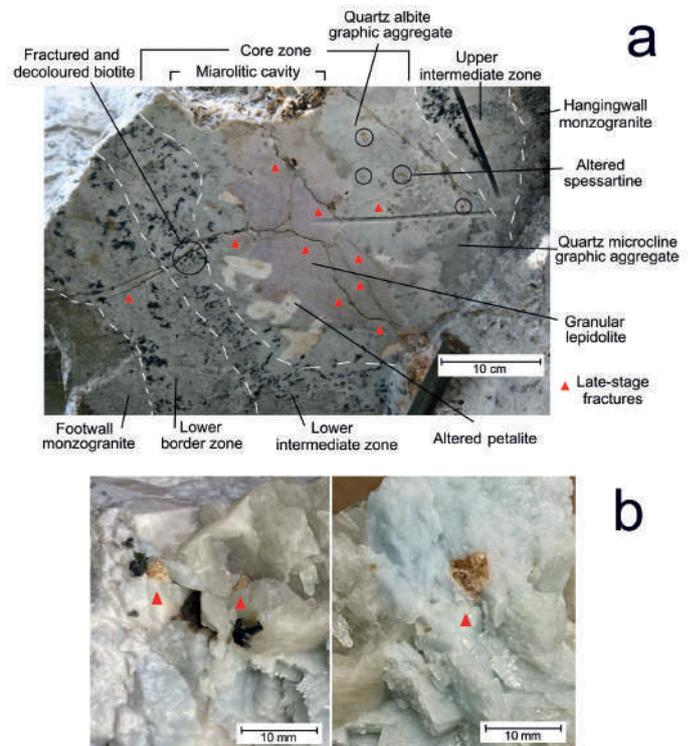

Figure 4 a) E-W section of the Rosina pegmatite (about 60 cm in thickness), with label for the different textures and mineralogical zonation. Altered cavity-lining minerals as well as late-stage fractures (red arrows) are also evidenced. Scale bar = 10 cm. b) Examples of heavily fractured and partially corroded spessartine crystals (red arrows) frozen in quartz and feldspars in proximity of cavities of the Rosina pegmatite. Crystals up to 6 mm in diameter. Scale bar = 10 mm.

cording to whether Fe and Mn totally or partially replace Li and Al. In the crystals from Elba, a partial substitution occurred at Y, according to the simplified mechanism $(1.5Li^+ + 0.5Al^{3+}) \leftrightarrow 2(Mn^{2+}, Fe^{2+})$. As this substitution determines a total charge variation, it needs to be balanced by a cation vacancy ($\square$) replacing Na at the X site: $Na^+ + (1.5Li + 0.5Al)^{\Sigma 3+} \leftrightarrow \square + 2(Mn,Fe)^{\Sigma 4+}$.

Results obtained, along with structural and paragenetic observation of the cavities in which the tourmaline samples were collected, provide evidence that the formation of the observed dark overgrowths is the result of an opening of the geochemical system ascribable to an event of pocket rupture. This event is further supported by the crystal-chemical features of an elbaitic multicolored tourmaline crystal, found in a wide miarolitic cavity naturally broken in two fragments and characterized by Mn-rich dark overgrowths, respectively purplish-red at the analogous pole and yellow-orange at the antilogous pole (Altieri et al., 2023). Based on the results obtained from this peculiar tourmaline crystal, the pocket rupture was responsible for its breakage, allowing for the formation of new growth surfaces in the direction of the analogous and the antilogous pole (Fig. 3).

Consequently, this crystal represents a key witness of the pocket rupture event registering not only the compositional variations of the geochemical system through the formation of Mn-rich overgrowths, but also the mechanical events that led to the crystal breakage, thus allowing for the formation of an unusual overgrowth at the antilogous pole. In the same study, a comparison of the overgrowths at the analogous and antilogous poles provides evidence of a preferential incorporation of elements at growth surfaces. Beside the preferential uptake of Ca, F and Ti at the antilogous pole, already described in literature (e.g., Henry & Dutrow, 1992; van Hinsberg

et al., 2006), we report for the first time a further preference at level of the ionic charge of the same element. In fact, OAS data show a selective uptake of Mn^{2+} at the antilogous pole, even in the presence of a considerable amount of Mn^{3+}, which preferred the analogous one. This uneven uptake of Mn ions resulted in the yellow-orange coloration of the antilogous overgrowth (Mn^{2+} dependent) rather than the purple-reddish color of the analogous overgrowths (Mn^{3+} dependent; Altieri et al., 2023).

Overall data obtained, as well as structural and paragenetic observations of the cavities in which the studied tourmaline crystals were collected, allowed to clearly correlate structural information (i.e., fracturing of the pocket and breakage of tourmaline crystals) to the late-stage tourmaline growth, and thus permitting definition a genetic model for the dark overgrowths in Elba tourmaline crystals. A pocket rupture event, probably related to thermal contraction during the cooling of the rock, led to mechanical brittle deformations of the enclosing pegmatite through the formation of late-stage fractures (Fig. 4a). This situation allowed the highly reactive late-stage cavity fluids to permeate the fractures surrounding the cavity where the early-crystallized Fe- and Mn-rich cavity-lining minerals were formed. Then, the hydrothermal alteration of such minerals through leaching and corrosion processes by the late-stage cavity fluids, led to the release of Fe and Mn in the system, thus causing a sudden change in the chemical composition of the pocket environment. These processes are supported by the oc-

currence of fractured and altered biotite crystals, as well as corroded spessartine garnet in the intermediate and lower border zone of the pegmatites (Fig. 4b).

Based on the size of the cavity, the extent of the fracturing phenomena and the consequent leaching processes, as well as the relative abundance of different primitive minerals in the enclosing pegmatite, the chemical composition of the residual cavity fluids underwent a variation in concentration in Fe and Mn. This can result in a simple color change up to a chemical evolution from an initial elbaite/F-elbaite composition to foitite, celleriite or schorl at the termination of the tourmaline crystals.

For instance, in the case of the "blue-cap" tourmalines, found in small pockets ($\sim$ 10 dm^3) within the San Silvestro and the Fucili veins (San Piero in Campo locality), compositional analyses revealed that the blue coloration of these crystals is exclusively related to a slight enrichment in Fe^{2+}. In addition, the presence of Fe only in the divalent state, suggests persisting reducing conditions in the pocket environment. This interpretation is consistent with a partial opening of the cavity system associated to minor fracturing phenomena, which led to a limited leaching of biotite crystals in the enclosing pegmatite (Altieri et al., 2022).

In other cavities, more extensive fracturing phenomena associated with the presence of abundant Fe/Mn-rich primitive minerals in the enclosing pegmatite, allowed the release of high amounts of Fe/Mn to the residual cavity fluids. In these conditions, a chemical evolution at the analogous termination of the tourmaline crystal occurred. Depending on the prevalence of Mn or Fe, the overgrowth can result in celleriite, $\square(Mn^{2+}_2Al)Al_6(Si_6O_{18})(BO_3)_3(OH)_3(OH)$, foitite, $\square(Fe^{2+}_2Al)Al_6(Si_6O_{18})(BO_3)_3(OH)_3(OH)$ or schorl, $NaFe^{2+}_3Al_6(Si_6O_{18})(BO_3)_3(OH)_3(OH)$ compositions.

A similar scenario occurred in a wide miarolitic cavity ($\sim$80 dm^3) of the Rosina pegmatite where a peculiar tourmaline crystal, found naturally broken in two fragments and characterized by late-stage Mn-rich overgrowths at both analogous and antilogous poles, was collected. In this case, a partial pocket collapse occurred, which caused an intense leaching of the primitive Mn-rich minerals in enclosing pegmatite. Although the Mn increase at the overgrowths is confirming a significant chemical evolution (MnO up to 7 wt%), the mineralogical species remain elbaite/F-elbaite, due to the lower presence of spessartine garnet in the enclosing pegmatite. This scenario was also responsible for the crystal to break, with the consequent formation of dark-colored overgrowths of purple-reddish color at the analogous poles (Mn^{3+} dependent), and yellow-orange at the antilogous ones (Mn^{2+} dependent). The presence of Mn in both +3 and +2 redox states suggests relatively oxidizing conditions during overgrowths formation (Altieri et al., 2023).

COMPOSITIONAL AND SPECTROSCOPIC CHARACTERIZATION OF GEM-QUALITY TOURMALINES FROM THE ALTO LIGONHA PEGMATITE DISTRICT (MAVUCO AREA, NE MOZAMBIQUE)

Main results

Sixteen tourmaline grains collected from the secondary deposit of Mavuco in the Alto Ligonha pegmatite district were studied. The samples collected were found as waterworn grains with a sub-angular to sub-rounded shape and most of them show a dark-colored prismatic overgrowth that surrounds completely, or in part, a multicolored core ranging from blue, green, yellow to purple-red, even within the same crystal (Fig. 5a). Compositional data were collected with electron microprobe along a straight traverse perpendicular to the c-axis with an average step size of 300 μm for a total of 501 spot analyses. To gain information on the mechanisms underlying the color displayed by the core regions of the tourmaline grains, OAS analyses in the UV-Vis region were performed on selected samples with particular chromatic features. The in-depth study on these tourmaline grains allowed a detailed characterization of their chemical composition, which was correlated to the color displayed.

Chemical data indicate that all studied samples are characterized by a CuO content that never exceeds 1 wt%. Despite the moderate concentration, Cu is able to contribute as color-causing agent especially in those core zones where its value approaches 1 wt%. Furthermore, EMP data revealed that most of the detrital tourmalines are of F-elbaite composition (Fig. 5b). This is the evidence that the tourmalines from the secondary deposit of Mavuco do not belong only to elbaite species, as assumed in previous studies (e.g., Laurs et al., 2008), but also to different species, including fluor-liddicoatite. A correlation study between chemical composition and color displayed by the studied tourmaline samples, allowed identifying the gemological variety to which the core zone of these grains belong. Specifically, in the secondary deposit of Mavuco, tourmalines belonging to indicolite, canary tourmaline, Paraiba-type and "Cu-bearing rubellite" varieties were identified.

Compositional analysis was extended to two tourmaline crystals from the "Marina" granitic pegmatite (MAV 21 and MAV 22 samples).

The presence of Cu in MAV 21 sample, which amount is comparable with that of the detrital tourmalines, supports the hypothesis that the "Marina" pegmatite represents a source from which the tourmaline grains of the Mavuco area were originated. Thus, the "Marina" pegmatite can be considered a primary deposit for Cu-bearing (Paraiba-type) tourmalines and its further exploration can be economically advantageous.
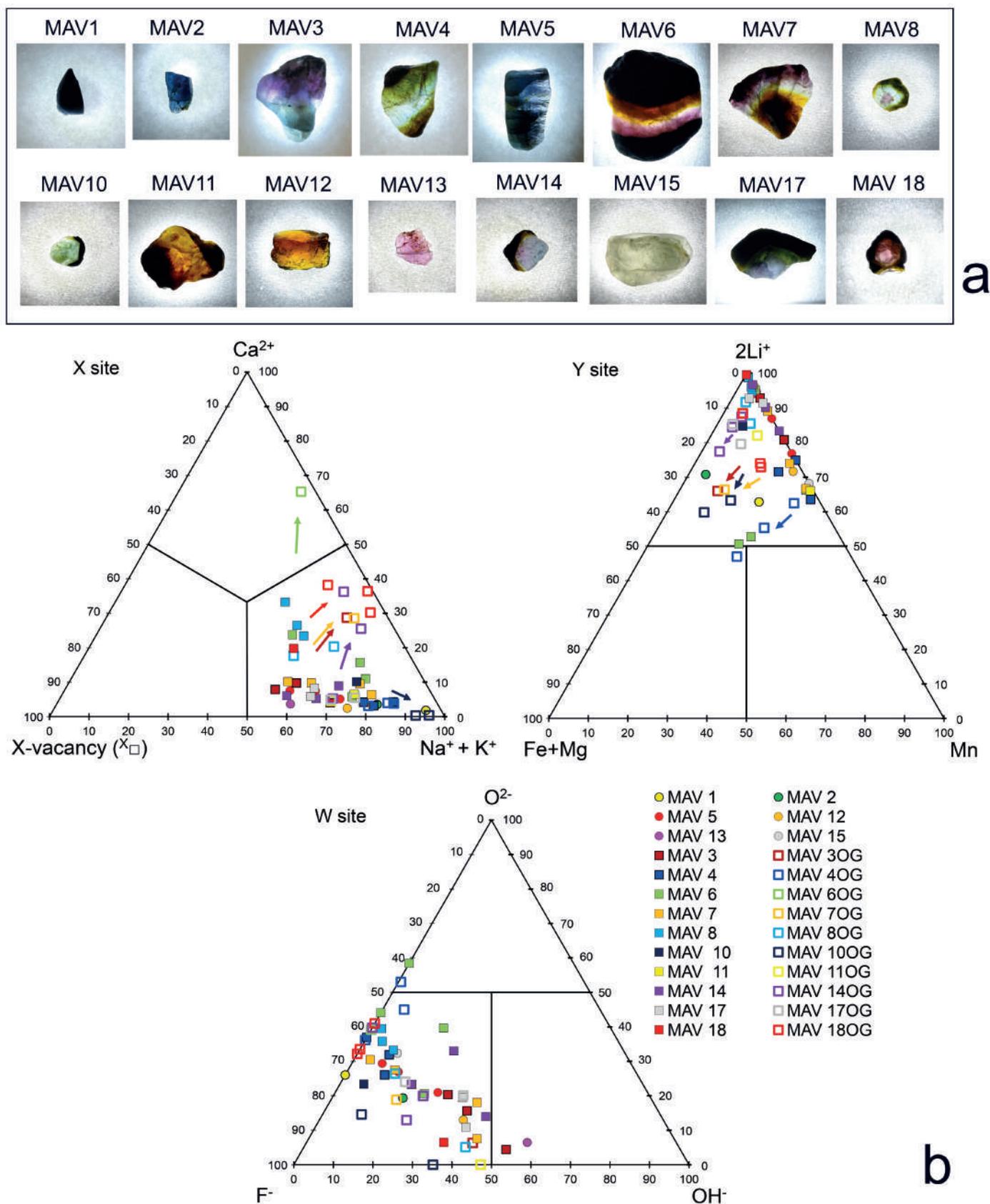
Figure 5 a) *The tourmaline grains analyzed for this study.* **b)** *Compositional diagrams based on the X-, Y- and W-site occupancy determined by EMPA. Each point represents the result in apfu of the core and overgrowth zones analyzed. Arrows highlight the compositional evolution trend from the core zone to the overgrowth observed in some of the analyzed tourmaline grains.*

The MAV 22 sample is characterized by a thick (up to 4 mm) black late-stage overgrowth developed all over the tourmaline surfaces, from the analogous to the anti-logous pole, including the prism faces, which chemical and morphological features are similar to those obser-ved in most of the detrital tourmalines from the secon-dary deposit of Mavuco (Fig. 6).

The presence of such an extended overgrowth further strengthen the hypothesis that "Marina" pegmatite is a primary source of the detrital tourmalines in the Mavuco area. Structural and paragenetic observations of the giant
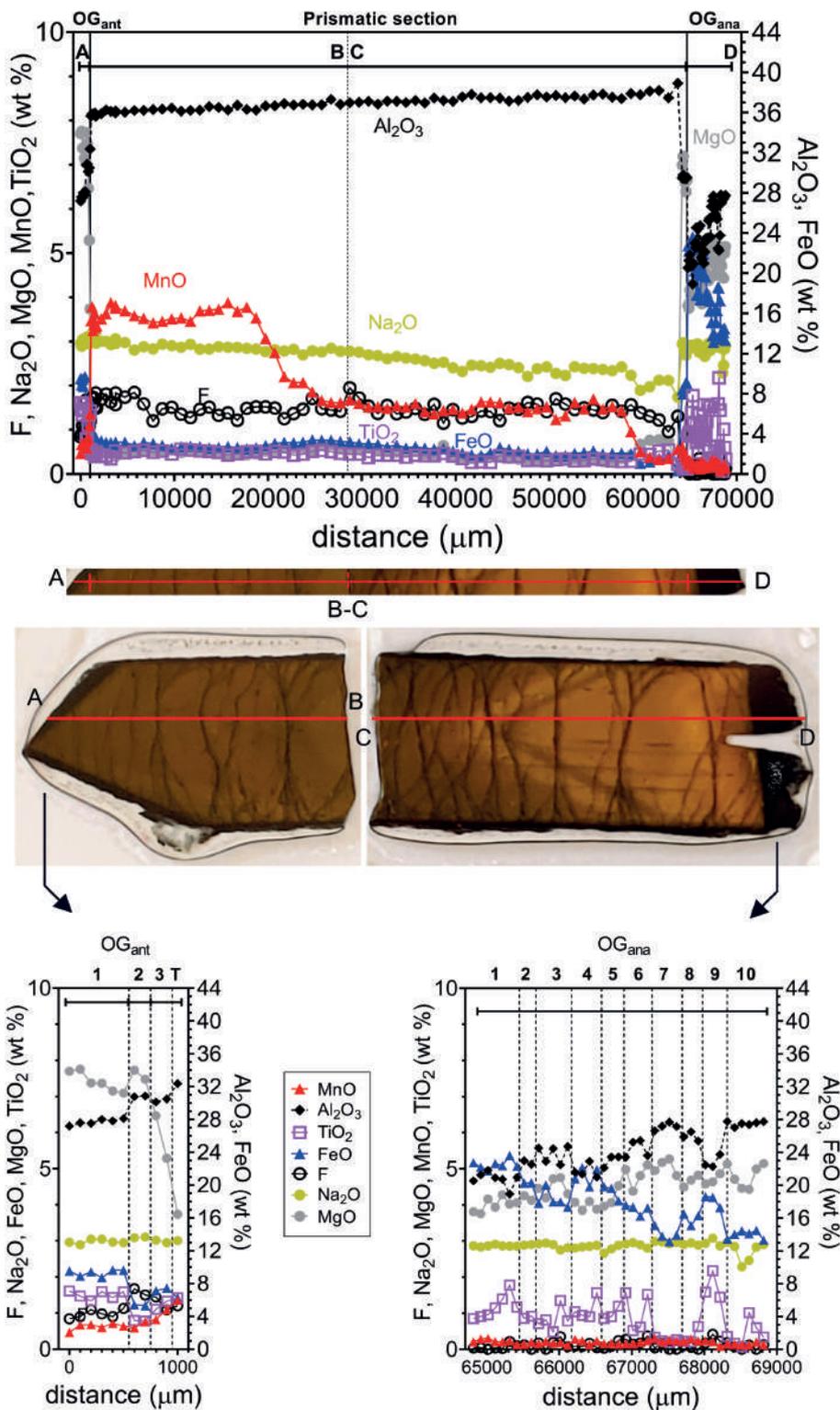
Figure 6 Upper panel: EMP analysis of the MAV 22 sample along a straight traverse parallel to the c-axis (only selected oxides are reported). Lower panel: close-up of the chemical composition of antilogous (OGant) and analogous (OGana) overgrowths in the MAV 22 sample (only selected oxides are reported).

cavity in which the MAV 22 sample was collected (about 12 m in size), provide evidences that the change in the chemical composition of the crystallization environment was related to an intense and widespread fracturing of the cavity, which culminated with the subsequent collapse of the pocket roof. In this scenario, the propagation of the fracturing phenomenon caused the collapse of the amphibolitic host rock, which reacted with the residual cavity fluids, thus releasing large amounts of Fe and Mg in the system (FeO up to 24 wt% and MgO up to 8 wt%). This condition, associated with a long lasting late-stage tourmaline crystallization ensured by B, which must be still present in the residual fluids of the cavity, allowed

for the development of a thick late-stage black overgrowth covering all over the crystal surfaces, including the prismatic faces and the steep pyramidal faces at the antilogous pole, which characterize the MAV 22 sample. In this case, the pocket collapse was associated to oxidizing conditions as supported by the high Fe^{3+}/Fe_{tot} ratio (> 0.50) observed at the analogous termination of MAV 22 sample. Moreover, the great availability of Fe and Mg in the system (FeO up to 24 wt% and MgO up to 8 wt%), allowed for a chemical evolution from an initial F-elbaite composition to a new Fe^{3+}-dominant species at the analogous overgrowth. Infact, chemical, spectroscopic and crystal-structure refinement resulted in a new mine-

ral species of the tourmaline supergroup, ferro-bosiite, ideally $NaFe^{3+}_3(Al_4Fe^{2+}_2)(Si_6O_{18})(BO_3)_3(OH)_3O$, recently approved by the IMA-CNMNC (proposal n. 2022-069) (Bosi et al., 2022b).

CONCLUSIONS

On the basis of results obtained from the chemical characterization of the detrital tourmalines from the Mavuco area, including those from the MAV 22 sample, as well as structural and paragenetic information of the cavity in which the MAV 22 sample was collected, it has been possible to extend the genetic model defined for Elba tourmalines to the prismatic overgrowths observed in the tourmaline crystals from the Alto Ligonha pegmatite district with some differences.

1) The size of the cavities. A larger size of the cavities, combined with extensive fracturing phenomena, may have played a key role in the formation of the prismatic overgrowths in the tourmaline crystals of the Alto Ligonha pegmatitc district. In fact, a broader fracturing surface may allow more extensive alteration and corrosion phenomena of the primitive minerals in the enclosing pegmatite by the late-stage fluids of cavity, leading to the formation of dark-colored overgrowths not only at the crystal termination, but also along the prismatic faces;

2) Typology of primitive minerals in the enclosing pegmatite. While biotite is the main Fe/Mg supplier in Elba pegmatitic system, biotite and especially ferromagnesian amphiboles are accounted for Fe/Mg supply in the petrogenetic systems of the Alto Ligonha district. In fact, the dramatic destabilizing event that characterizes the cavity in which the MAV 22 sample has been collected, allowed the cavity-fluids to react with the collapsed amphibolithic host rock, with the consequent release of greater amounts of Fe and Mg in the system.

Concerning the Mn availability, in the petrogenetic system of Elba Island, spessartine garnet is responsible for both depletion and release of Mn in the crystallization environment, being the main regulator of Mn levels during the evolution of the pegmatitic system. This is consistent with the low content in Mn recorded in the early-stages of tourmaline crystallization, because of the high degree of Mn incorporation in spessartine garnet. On the other hand, spessartine etching results in high availability of Mn in the pocket environment, with the consequent formation of unusual Mn-rich dark-colored overgrowths. In contrast, in the petrogenetic system of the Alto Ligonha, the scarce presence of spessartine garnet in the secondary deposit of Mavuco suggests that the main regulator of Mn levels during crystallization of tourmaline is apatite. However, apatite is a fairly-competitive mineral for Mn respect to spessartine. This can explain the higher content in Mn recorded in the core

zones of the analyzed detrital tourmalines and the lower increase at the overgrowth right after the pocket rupture event. Also, the presence of apatite in the host rock can explain the release of Ca during the cavity opening, as observed in some overgrowths.

The results obtained in this Ph.D research allowed to define and validate a model for the genesis of the dark-colored overgrowths in pegmatitic gem- tourmaline crystals from Elba Island. This model has been applied to the prismatic overgrowths of the tourmaline crystals from the Alto Ligonha pegmatite district, and can be further extended to explain the late-stage color and composition anomalies of gem-tourmaline crystals in many other gem-pegmatite deposits in the world.

REFERENCES

Altieri, A., Pezzotta, F., Skogby, H., Hålenius, U. & Bosi, F. (2022): Blue-growth zones caused by Fe²⁺ in tourmaline crystals from the San Piero in Campo gem-bearing pegmatites, Elba Island, Italy. *Mineral. Mag.*, **86**, 910-919.

Altieri, A., Pezzotta, F., Skogby, H., Hålenius, U. & Bosi, F. (2023): Dark-coloured Mn-rich overgrowths in an elbaitic tourmaline crystal from the Rosina pegmatite, San Piero in Campo, Elba Island, Italy: witness of late-stage opening of the geochemical system. *Mineral. Mag.*, **87**, 130-142.

Bosi, F., Pezzotta, F., Altieri, A., Andreozzi, G.B., Ballirano, P., Tempesta, G., Cempírek, J., Škoda, R., Filip, J., Čopjaková, R., Novák, M., Kampf, A.R., Scribner, E. D., Groat, L.A. & Evans, R.J. (2022a): Celleriite, □(Mn²⁺₂Al) Al₆(Si₆O₁₈)(BO₃)₃(OH)₃(OH), a new mineral species of the tourmaline supergroup. *Am. Mineral.*, **107**, 31-42.

Bosi, F., Altieri, A., Skobgy, H., Pezzotta, F., Hålenius, U., Tempesta, G., Ballirano, P., Flégr, T. & Cempírek, J. (2022b): Ferro-bosiite, IMA 2022-069. CNMNC Newsletter No. 70, December 2022. *Eur. J. Mineral.*, **34**, 591-601, 2022.

Henry, D.J. & Dutrow, B.L. (1992): Tourmaline in a low grade clastic metasedimentary rocks: an example of the petrogenetic potential of tourmaline. *Contrib. Mineral.*, **112**, 203-218.

Laurs, B.M., Zwaan, J.C., Breeding, C.M., Simmons, W.B., Beaton, D., Rijsdijk, K.F., Befi, R. & Falster, A.U. (2008): Copper-bearing (Paraiba-type) tourmaline from Mozambique. *Gems. Gemol.*, **44**, 4-30.

Pezzotta, F. (2021): A history of tourmaline from the Island of Elba. *Mineral. Rec.*, **52**, 669-720.

van Hinsberg, V.J., Schumacher, J.C., Kearns, S., Mason, P.R.D. & Franz, G. (2006): Hourglass sector zoning in metamorphic tourmaline and resultant major and trace-element fractionation. *Am. Mineral.*, **91**, 717-728.