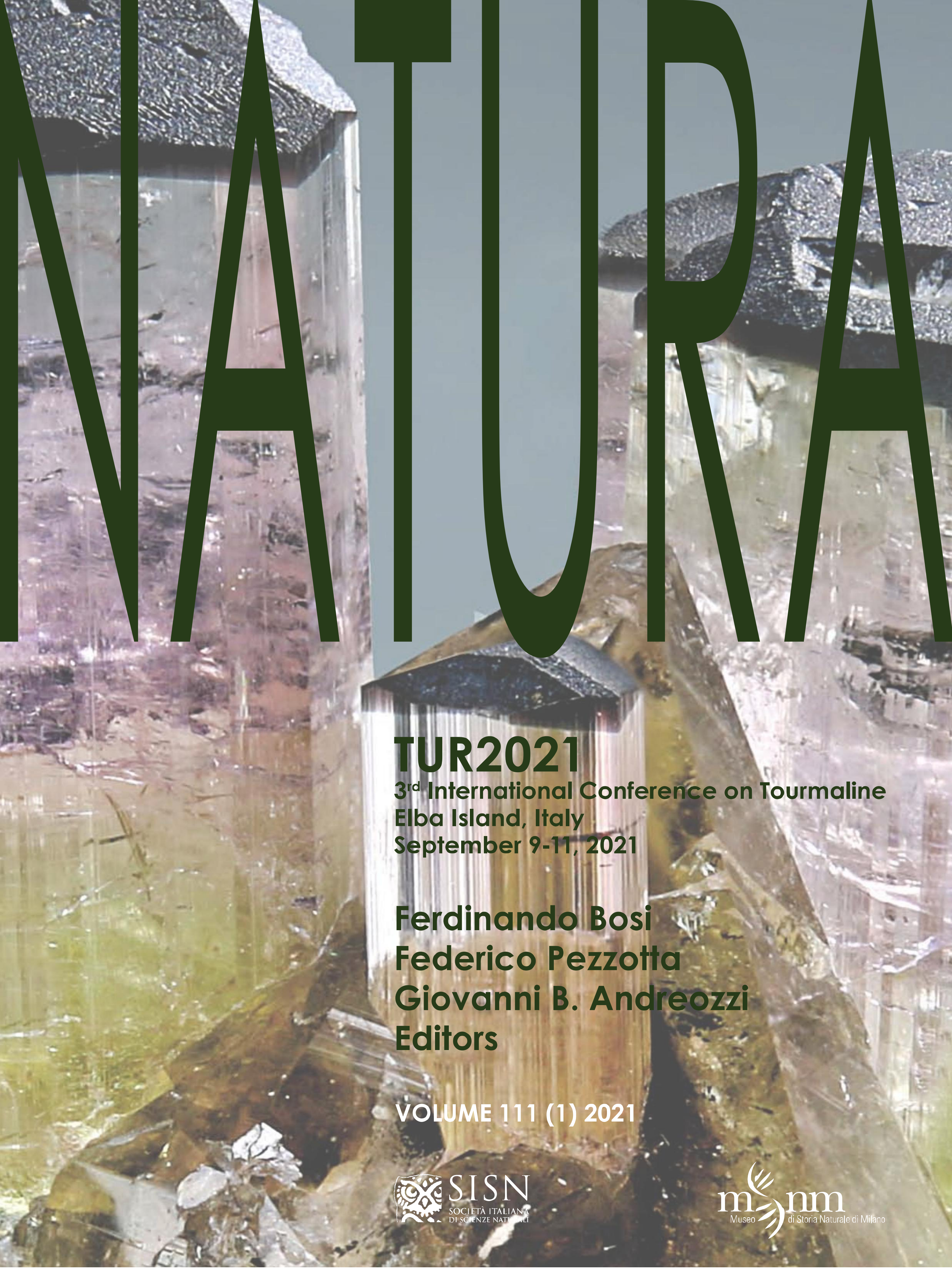

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September 9-11, 2021

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In copertina Tourmaline crystals with quartz and "lepidolite", Grotta d'Oggi, Elba Island. (Photo A. Miglioli).

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TUR2021

3rd International Conference on Tourmaline

This volume contains 52 abstracts and keynote abstracts presented at the 3rd International Conference on Tourmaline (*TUR2021*), held on Elba Island, Italy, from 9 to 11 September 2021 (https://www.tur2021.com).

The Conference has been organized along with the sponsorship of SIMP (Italian Society of Mineralogy and Petrology), and support of the Sapienza University of Rome and Natural History Museum of Milan.

The abstract volume is the joint effort of all conference participants and covers many aspects of tourmaline regarding the latest discoveries across the range of crystallography, mineralogy, petrology, geochemistry, isotopic analyses, ore-deposits research, gem science, and much more.

All the abstracts published in this volume were critically read and approved by the scientific committee for presentation at *TUR2021*.

We wish to express our deepest gratitude to the members of the scientific committee of *TUR2021*: J. Cempírek, (Masaryk University), A. Dini (National Research Council of Italy), B.L. Dutrow (Louisiana State University), A. Ertl (University of Vienna), D.J. Henry (Louisiana State University), H.R. Marschall (Goethe University Frankfurt), M. Novák (Masaryk University), R.B. Trumbull (Helmholtz Centre Potsdam-GFZ), V.J. van Hinsberg (McGill University, Montreal).

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Ferdinando Bosi
Federico Pezzotta
Giovanni B. Andreozzi
(Co-chairmen of *TUR2021*)

Towards tourmaline REE pattern explanation

Oleg Vereshchagin[1]*, Sergey N. Britvin[1], Bernd Wunder[2], Olga Frank-Kamenetskaya[1], Franziska D. H. Wilke[2]

Natural tourmalines could contain sufficient amounts of rare earth elements (up to ~1000 ppm; Bačík *et al.*, 2012), exhibit both positive and negative Eu anomalies (Čopjaková *et al.*, 2013) and are characterized by different light / medium / heavy rare earth elements (REE) ratios (Gadas *et al.*, 2012). Even though REE patterns of natural tourmalines were studied for decades, no direct information on REE speciation in tourmaline and factors affecting REE pattern are available. Exploring the way lanthanides incorporate in tourmaline structure one could get both new functional materials and explain REE patterns of natural tourmalines.

In the course of current work we report on synthetic REE^{3+}- tourmalines (REE^{3+} = La, Nd, Eu, Yb) and discuss the role of the *X*-site cations.

REE^{3+}- tourmalines were synthesized in 11 experiments at temperatures of 700 °C and pressures of 0.2 (Fig. 1) or 4.0 GPa. Besides *REE*-tourmaline, other REE borates were obtained (<10 vol. %;): $REEAl_{2.07}(B_4O_{10})O_{0.6}$ in La-, Nd- and Eu-synthesis, $REEBSiO_5$ (stillwellite-like compounds) in La- and Nd-synthesis, $Eu_2B_2SiO_8$ and $YbBO_3$. In Yb-synthesis $Yb_2(Si_2O_7)$ (keivyte-(Yb)) was also obtained.

Elongated or needle-like prismatic tourmaline crystals from high-pressure experiments are much smaller (up to 0.5×6 μm) than those from the low-pressure experiments (up to 100×300 μm).

Based on elemental analysis data we have found that REE-content in tourmalines varies significantly (0.05 - 1.05 atoms per formula unit (apfu)) with Yb<La≤Nd<Eu independent of the pressure conditions. REE-content in tourmalines, obtained at low pressure, is 2-3 times higher than that obtained from high-pressure experiments. The Nd- and Eu-tourmalines exhibit cathode- and photoluminescence properties, which confirm their trivalent oxidation state. Single-crystal X-ray diffraction data show that Eu^{3+} and Nd^{3+} occupy the 9-coordinated *X*-site in the tourmaline structure (Table 1).

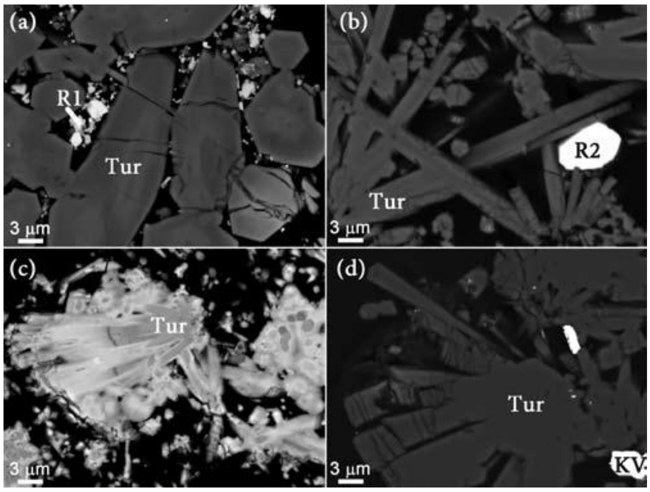

Fig. 1 - BSE images of REE-tourmalines (Tur), obtained at low pressure (2 kbar): (a) La-tourmaline and $LaBSiO_5$ (R1), (b) Nd-tourmaline and $NdBSiO_5$ (R2), (c) Eu-tourmaline, (d) Yb-tourmaline and $Yb_2(Si_2O_7)$ (KV).

Our investigations indicate pressure effect and crystal-chemical constraints on REE incorporation in tourmalines, which is of great importance for geoscientific implications.

It was suggested that the dominant factor governing the species of REE is temperature (e.g., Sverjensky, 1984). Our data on synthetic tourmalines, obtained at same temperature (700 °C) but at different pressures (0.2 / 4.0 GPa), clearly show that additional pressure could be a main factor, affecting tourmalines REE pattern.

It was also proposed that significant enrichment of heavy REE in tourmaline (in contrast to the REE patterns of the whole-rock samples) indicates a mobilization of heavy REE during hydrothermal processes (Yavuz *et al.*, 2011). However, according to our data predominance of

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light and medium REE (e.g., Eu, Nd, La) over heavy REE (Yb) in tourmalines, could be due to tourmaline crystal structure constrains, not crystallisation medium effects.

Preliminary experimental data on trace-element partitioning between tourmaline and silicate melt (van Hinsberg, 2011) predicted that Eu^{2+} is the preferential valence state in the tourmaline crystal structure and Eu^{3+} occur at octahedral sites. We have found that (1) the tourmaline crystal structure can accommodate REE as trivalent cations; and (2) REE^{3+} cations are located at the 9-coordinated *X*-site. The latter is also in a good agreement with published data, as Eu^{3+} is not even observed as six-coordinated polyhedral (Gagné *et al.*, 2018). Besides that, we can conclude that tourmalines could be a phase that concentrates REE during crystallization process, as total amount of REE^{3+} can reach amounts up to 1 apfu.

It is worth to note, that the REE^{+} valence state (e.g., Eu^{3+} or Eu^{2+}) depends on the redox conditions at which tourmaline formed and that Eu^{2+}-rich tourmaline should not be completely excluded for natural occurrence. Our data do not exclude the prediction, that divalent rare-earth cation could occur at the *X*-site as REE^{2+} cations are even larger than REE^{3+} cations.

Additionally, one might conclude that natural tourmalines could contain other trivalent cations at the *X*-site (e.g., Bi^{3+}; Ertl & Bačík, 2020) and that the general classification scheme for tourmaline group may be expanded, as not only monovalent (e.g., Na, K, Li, Ag, NH_4) and divalent (e.g., Ca, Sr, Pb), but also trivalent cations could occupy this site.

Table 1 - Variations of *X*-site occupancies of natural and synthetic tourmalines.

No	*a*, Å	*c*, Å	X_{0-1}	<*X*-O>, Å	Y_3	<*Y*-O>, Å	Z_6	<*Z*-O>, Å	Reference
1.	15.903(5)	7.168(3)	$\square_{0.72}Eu^{3+}_{0.28}$	2.708	$Al_{1.74}Mg_{1.26}$	1.990	$Al_{5.22}Mg_{0.78}$	1.927	Eu-tourmaline
2.	15.8934(15)	7.1304(7)	$\square_{0.83}Nd^{3+}_{0.17}$	2.705	$Al_{1.95}Mg_{1.05}$	1.979	$Al_{5.28}Mg_{0.72}$	1.922	Nd-tourmaline
3.	15.910(1)	7.131(1)	$\square_{0.91}Na_{0.09}$	-	$Al_{1.62}Mg_{1.38}$	1.992	$Al_{4.92}Mg_{1.08}$	1.920	Berryman *et al.*, 2016

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