1. Research activity (max 1.000 words)

Towards a crystal-chemical model for revealing the origin and evolution of gem-quality tourmalines

Research objectives

The focus of this project is the definition of a crystal-chemical model of gem-quality tourmalines aimed at reconstructing their origin, chemical evolution and growth process. To achieve this objective, selected gem-quality tourmalines (e.g. *rubellite* and *paraiba* mineral varieties) from Mozambique, Madagascar and Elba Island pegmatitic dikes will be used as a case study and microchemical, structural, spectroscopic and isotopic investigations will be applied as experimental approach.

As a possible implication, since tourmaline is an excellent petrogenetic indicator (being able to record the events that affected the environment in which they formed), this study fits into a broader context whose general objective is the reconstruction of the chemical and P-T conditions of the pegmatitic system formation.

State of the art

Tourmalines are the dominant host for B in most rocks of the Earth crust and represent a supergroup of minerals, possessing a significant chemical variability containing both light and heavy elements (from H to Pb) which is reflected in 33 different mineral species.

As tourmaline can incorporate a wide variety of elements, with Fe and Mn at different oxidation state, it very efficiently records the chemical composition of the system including the redox conditions during the crystallization process. Tourmaline crystals are also sensitive to physicochemical changes in the environment and, even from a single grain, this is noticeable by the presence of typical color zoning along the crystal which testifies a change in the crystallization fluid composition, due to a reopening of the system. Because of its stability over a significant P-T range and the extremely low rates of volume diffusion for major and trace elements in its structure, tourmaline can retain original chemical and textural information. The highly variable chemical composition, including B isotopes, and the refractory behavior make tourmaline an extremely useful mineral for Geosciences and nature's perfect forensic mineral. Its detailed crystal-chemical characterization may allow revealing the type of the petrological and geodynamic environment in which tourmaline crystal grew.

Tourmalines are also notorious for the wide spectrum of colors they appear, even within individual crystal, ranging from colorless, through red, pink, yellow, orange, green, blue and violet, to brown and black. The transition elements $Fe^{2+/3+}$, $Mn^{2+/3+}$, Ti^{4+}, Cu^{2+} and V^{3+} act as important color-causing chromophores occupying the Y and Z octahedral sites, influencing color and color intensity through both crystal-field transitions (CFT) and intervalence change transfer interactions (IVCT). However, the interactions at a structural level causing the color as well as the relationship between color and chemical composition of tourmaline are not yet completely clear.

Rubellite and *paraiba* from pegmatitic dikes of Brazil, Nigeria, Mozambique, Madagascar and Elba Island are among the most renowned gem-quality tourmalines for the combination of color, durability and rarity. These features make them unique from a gemological viewpoint and therefore with a high commercial value, limiting the information regarding their crystal-chemical characteristics. For example, few data are available on a detailed chemical analysis including isotopic and trace elements of Madagascar tourmalines, which has not

yet been performed. Moreover, a correlation study between UV-Vis-Nir absorption spectra and structural information obtained by FTIR and Raman analysis as well as an in-depth study of the atomic mechanisms that regulate tourmaline color appearance have never been done so far. To fill this gap, selected gem-quality tourmaline samples from Mozambique, Madagascar and Elba Island will be studied in this PhD project for a detailed crystal-chemical and isotopic study of the tourmaline, including the color mechanisms. This will also contribute to get information on the pegmatite from which tourmalines were originated.

Work plan

Gem-quality tourmaline samples from Mozambique, Madagascar and Elba Island will be provided by ongoing mining projects. Some samples come from Anjanabonoina and Ibity Valley (Antananarivo, Madagascar) and Befisiotra (Fianarantsoa, Madagascar), respectively, others come from Mavuco (Alto-Ligonha, Mozambique), the world's largest known alluvial deposit of Cu- bearing tourmalines. Elba Island samples come from San Piero in Campo and Sant'Ilario in Campo.

Selected tourmaline samples will be subjected to a detailed analysis including:

- Chemical and isotopic analysis (by means of EMP, LIBS, SIMS and MS)
- Crystallographic and spectroscopic analysis (by means SCXRD, FTIR, Raman and UV-Vis-Nir spectroscopy)

All these analyses will provide the most detailed experimental information on the chemical composition and short- and long-range crystal-structure of the studied tourmalines, which in turn will be related to the tourmaline color and the pegmatite from which they formed.

Selected tourmaline samples will be also subject to heat treatment under controlled conditions to observe any color change and those showing a color change will be re-analyzed by UV/Vis/NIR, FTIR and Raman spectroscopy.

Implications and applications

This project can have several implications and applications. First of all, the crystal-chemical model developed in this study can be extended to any gem-quality tourmaline of different provenance and help the reconstruction of P-T conditions of pegmatitic systems evolution. From a gemological viewpoint, the color displayed by gem-quality tourmalines is an important commercial characteristic and its alteration may have relevant consequences on the economic value of tourmaline. Specifically, it should be noted that the characteristic blue "neon" and pink-red colors of *paraiba* and *rubellite* (respectively) can be induced by thermal treatment. Thus, the information obtained by UV/Vis/NIR, FTIR and Raman spectroscopy may be used to experimentally distinguish, through the identification of specific spectroscopic characteristics, whether their color is natural or artificial. From a mining geologic viewpoint, the comparison of data obtained from Cu-bearing tourmalines occurring in the residual and colluvial secondary deposit of Mavuco (Mozambique) with those obtained from samples occurring in a recently discovered primary pegmatitic field will allow establishing whether the exploitation of this new mining field is economically advantageous. This may have a significant impact on the Gross Domestic Product of Mozambique country. Finally, the detailed information on the crystal structure, chemical and isotopic composition of the studied tourmalines will be used to reconstruct the evolution history of the Mozambique, Madagascar and Elba Island pegmatites as well as to compare gem-quality tourmalines of different provenance.

2. Research products

a) Publications (ISI journals)
b) Publications (NON ISI journals)
c) Manuscripts (submitted, in press)
d) Abstracts