



# Crystal chemical and structural peculiarities of staurolite from rocks undergone different metamorphic evolution: FTIR spectroscopy study

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## Introduction

Estimation of the metamorphic conditions is one of the main purposes of the petrological investigations of metamorphic rocks. However, due to the overprinting of metamorphic events sometimes no mineral pairs or mineral parageneses are preserved, allowing the use of conventional thermobarometers or single mineral calibrations. In these cases, the investigators are forced to find appropriate properties in only one mineral, which are sensitive to P-T conditions. This study is a first attempt to use the crystal chemical peculiarities of staurolites for these purposes. As a first step we compare staurolites from three regions with different metamorphic history and study their crystal chemical peculiarities on the ground of their FTIR spectra and EMPA data.

## Sample location and chemical composition

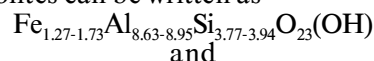
Samples from three regions differing in their metamorphic evolution are selected — metapelites from the region of Biala Reka (East Rhodopes), (sampl. Nb. L-431, L-662a and L-754 and hereafter denoted L-series), orthoschists from the region of Ograzhden Mountain (sampl. M-20, M-252 and M-259 and hereafter denoted M-series) as well 1 sample from the metapelites of the Ustrem formation in Sakar Mountain (Čatalov, 1985), (sample C-1, hereafter denoted C-series). For the first region the metamorphic history has been well established (Macheva, 1998) with clockwise P-T-t path — an early HP/LT episode ( $P_{\min} \approx 13$  kbar and  $T \approx 450^\circ\text{C}$ ), related to rapid crustal thickening followed by isothermal decompression (MT/MP —  $P = 9-3$  kbar and  $T \approx 550^\circ\text{C}$ ) and a final cooling episode of LT/LP type ( $P = 3-2$  kbar and  $T \approx 400^\circ\text{C}$ ). Staurolite was formed during the entire MT/MP episode.

The samples from Ograzhden Mountain are selected from orthoschists, in which relic kyanite and

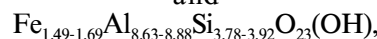
garnet are preserved. The calculated metamorphic conditions for this metamorphic episode are  $T \approx 670^\circ\text{C}$  and  $p_{\min} = 7$  kbar. Staurolite and chloritoid are formed at  $T_{\max} \approx 550^\circ\text{C}$  after almost entirely sericitized kyanite porphyroblasts.

Metamorphic conditions for the staurolite-bearing rocks of the Ustrem formation in Sakar Mountain as estimated by Чаталов, Грозданов (1978) are  $T \approx 450-600^\circ\text{C}$  and  $P = 1.8-6$  kbar.

EMPA data on staurolites from L-series and from M-series do not show any remarkable differences in their chemistry. The generalized formula of the studied staurolites can be written as



and



respectively. They are unzoned, Fe-rich, with a  $\text{Fe}_{\text{tot}}/(\text{Fe}_{\text{tot}} + \text{Mg})$  ratio of 0.72-0.85 and 0.77-0.82, respectively, Ti-poor (0.2-0.10 p.f.e.) and with ZnO content in the range 0-1.59 and 0-0.75 for L and M-series, respectively. EMPA of the staurolites from C-series were not done. The similarity in the chemical composition of the staurolites from the three regions does not allow making any inferences about the metamorphic conditions, regardless the differences in petrographical observations. Because of that, we have undertaken an FTIR study of the mineral.

## FTIR spectroscopy measurements

An unpolarized FTIR absorption spectroscopy was applied for investigation of local structural peculiarities of staurolite. The measurements are performed on the Bruker TENSOR-37 FTIR spectrometer in the range  $4000-400\text{cm}^{-1}$ . Standard KBr micropellets preparation technique with sample/KBr weight ratio of 0.01 was used for the powder measurements in the mid-IR region. The spectra were obtained at room temperature with the resolution of  $4\text{ cm}^{-1}$  from 72 scans.

The staurolite, as other orthosilicate minerals, could be differentiated by their mid-infrared spectra through a study of the bands due to (O-H) and (Si-O) groups. In the (O-H, H<sub>2</sub>O) stretching region (3800–3200 cm<sup>-1</sup>) of the IR-spectrum few close and partially mixed bands due to O-H group asymmetric and H<sub>2</sub>O symmetric and asymmetric stretching vibrations (3400–3200 cm<sup>-1</sup>) are distinguished. The isolated OH<sup>-</sup> ion has a single stretching band in the 3757 cm<sup>-1</sup> region. The non-isolated O-H groups in staurolites could involve atoms in different structural positions (Koch-Müller et al., 1997). The frequency changes of the O-H group in crystalline solids depend on the strength of the H-O-X bonds and

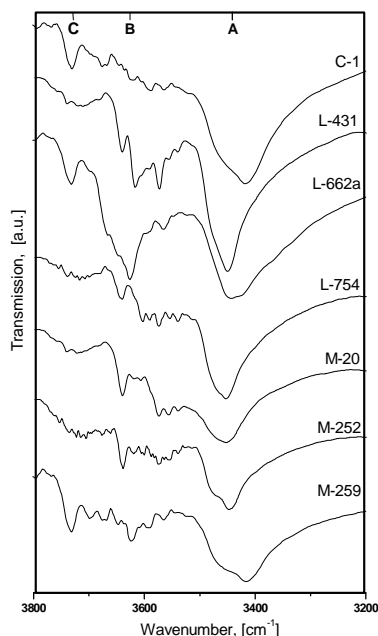


Fig. 1. O-H region of the staurolite spectra of samples from: C (Sakar), L (East Rhodopes) and M (Ograzhden)

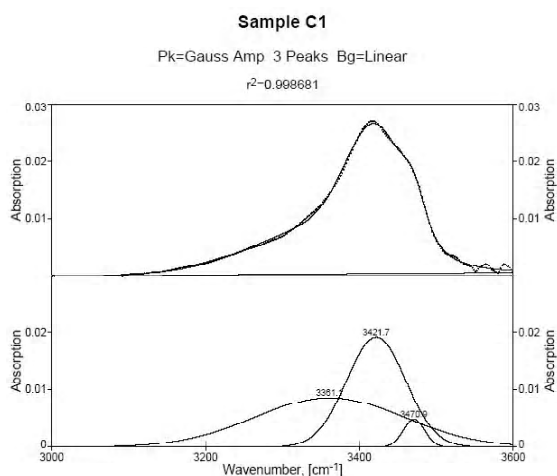


Fig. 2. The staurolite O-H A-band structure presented by convolution of single Gaussian functions for C1 sample

could be related to variations in the O-H and O-X bond lengths as well as to H-O-X bond angles.

Strong stretching vibration band of the SiO<sub>4</sub> tetrahedral group, which is typical silicate structural unit, usually occurred in the wavenumber range 1200–900 cm<sup>-1</sup>. The ideal SiO<sub>4</sub> tetrahedral configuration possesses T<sub>d</sub> cubic point symmetry and according irreducible group representation one triply degenerated (both infrared and Raman active) asymmetric stretching vibration mode  $\nu_{3as}$  occurred in this range. In the rock forming orthosilicates the symmetry of the SiO<sub>4</sub> tetrahedron is often far from ideal T<sub>d</sub> and its reducing leads to decreasing the degeneracy of the mentioned strong vibration mode. The way of T<sub>d</sub> symmetry violation could be different. In the natural formed staurolites it is usually due to Al→Si heterovalent isomorphism, which lead to increase of the (Si-Al)-O distance. In this case, because of enlargement of the tetrahedral sizes, the  $\nu_{3as}$  vibration mode shifts to the lower frequencies. The symmetry distortions of the SiO<sub>4</sub> tetrahedra close to Al→Si atom replacement lead to band splitting and peak intensity decreasing. The existence of several different types of tetrahedral distortions, especially when they occurred in the same unit cell, is another way for appearing new vibration bands in this region of the vibration spectrum.

The infrared spectra in the range 3800–3200 cm<sup>-1</sup> of studied staurolites are shown on fig. 1, where the (O-H, H<sub>2</sub>O) stretching region of mid-IR spectrum is presented. Three different bands marked A, B and C are distinguished: (i) broad and relatively strong A-band in the range 3500–3300 cm<sup>-1</sup> with maximum close to 3400 cm<sup>-1</sup>; (ii) weak B-band at about 3650 cm<sup>-1</sup>; (iii) weak C-band centered around 3750 cm<sup>-1</sup>. All three bands could be assigned to asymmetric stretching modes of O-H groups in different structural positions. A pronounced A-band broadening and intensity decreasing in the spectra from M-series in comparison to these of L-series are observed. The A-band has composite structure, which could

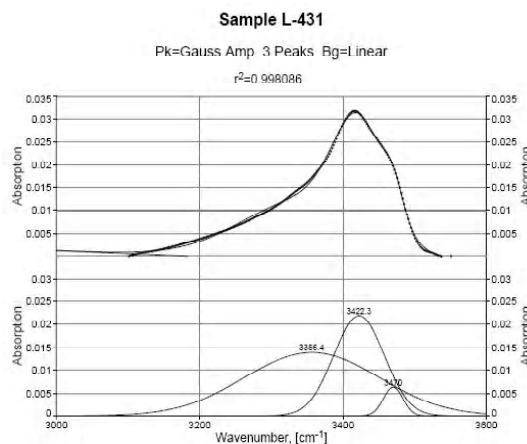


Fig. 3. The staurolite O-H A-band structure presented by convolution of single Gaussian functions for L-431 sample

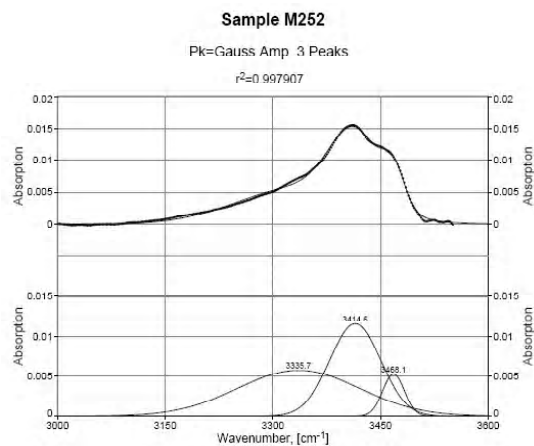


Fig. 4. The staurolite O-H A-band structure presented by convolution of single Gaussian functions for M-252 sample

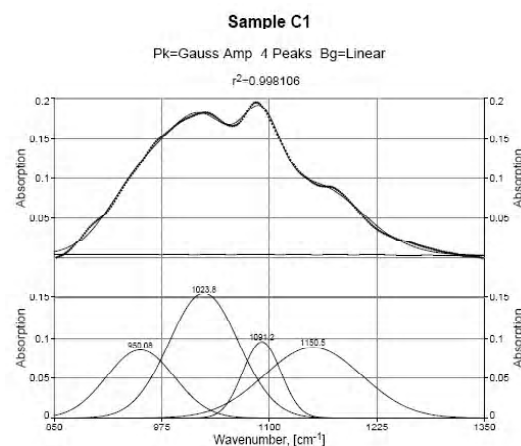


Fig. 6. The SiO<sub>4</sub> region of staurolite spectrum of C1 sample deconvoluted into single Gaussian functions

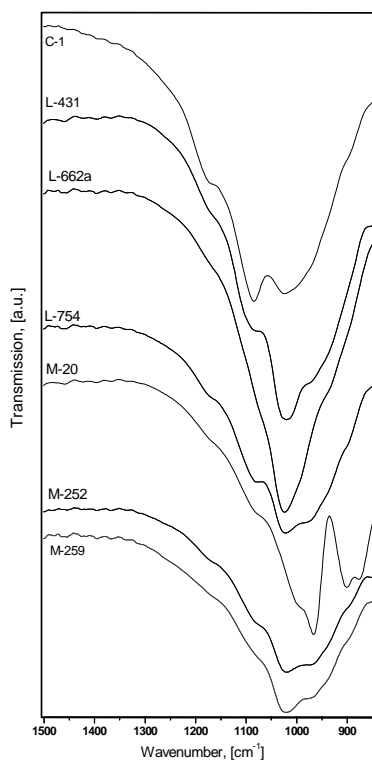


Fig. 5. SiO<sub>4</sub> region of the staurolite spectra of samples from: C (Sakar), L (East Rhodopes) and M (Ograzhden)

be deconvoluted into single Gaussian functions as is shown in the fig. 2-4. The B and C bands could not be unambiguously presented in that way, due to registered low S/N ratio.

The staurolite infrared spectra measurements in the range 1500-850 cm<sup>-1</sup> assigned to  $\nu_{3as}$  vibration mode of the SiO<sub>4</sub> tetrahedral group are shown on fig. 5. The deconvoluted SiO<sub>4</sub> band structures are presented on the fig. 6-8. A band broadening and band intensity decreasing in the spectra from M-series comparatively to L-series are distinguished.

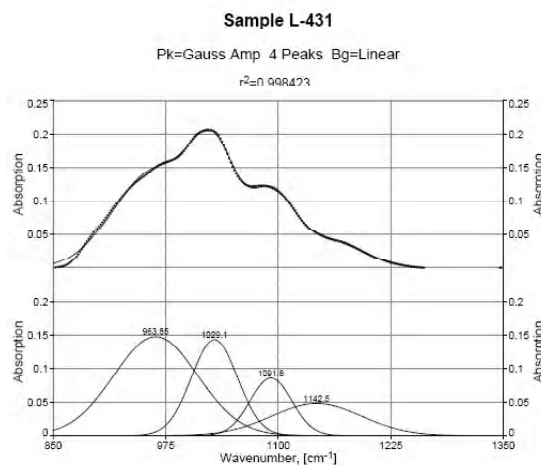


Fig. 7. The SiO<sub>4</sub> region of staurolite spectrum of L-431 sample deconvoluted into single Gaussian functions

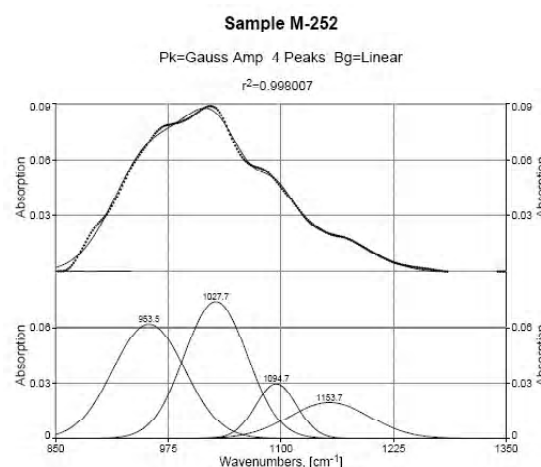


Fig. 8. The SiO<sub>4</sub> region of staurolite spectrum of M-252 sample deconvoluted into single Gaussian functions

## Discussion and conclusions

The presented FTIR spectra of staurolites from the three studied regions show some similarities but differences in their thin band structures are also observed. The pronounced decreasing the intensity of A-band in the OH-region of the spectrum for Ograzhden staurolite samples in comparison with those from E Rhodopes is established (fig. 1-4). This effect could be attributed to differences in the P-T conditions of the metamorphism. The significant variations of IR spectra of staurolites from the Biala Reka region (E Rhodopes) in the range 3800-3200  $\text{cm}^{-1}$  could be related to the formation of the mineral during the entire process of isothermal decompression ( $P = 9-4$  kbar and  $T \approx 550^\circ\text{C}$ ) as is ascertained by the petrological investigations. This region shows a great variety in bands intensity as well as in their broadening because of the large variations in fluid supply during rock exhumation. Based on petrological con-

siderations as well as on the peculiarities observed on the IR spectra in the OH range, an assumption could be made that the staurolites from Ograzhden Mountain formed at higher temperature, but in more limited interval. The OH A-band of spectrum obtained from Sakar Mountain staurolite sample is close to these from Biala Reka.

The thin structure of staurolite vibration spectra in the asymmetric stretching vibration  $\nu_{3as}$  region presented on fig. 5 could be assigned to the heterovalence Al  $\rightarrow$  Si isomorphism in T1 structural positions. Because of larger Al ion radius, with the pressure increasing, a decrease of Al  $\rightarrow$  Si substitution in T1 is expected. This process is reflected in shifting of the  $\sim 1020$   $\text{cm}^{-1}$  main peak position to higher frequencies (fig. 6-8). The total increase of band intensity in spectra from Biala Reka-series is also expected. This effect could be partially reduced with increasing the disorder of  $\text{SiO}_4$  tetrahedra deformation due to the formation at higher-pressure conditions.

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## Кристалохимични и структурни особености на ставролит от скали, претърпели различна метаморфна еволюция: изследване с FTIR спектроскопия

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**Резюме.** Изследвани са ставролити от метапелити и ортошисти от 3 района — Бяла река (Източни Родопи), Огражден планина и Сакар. Получените FTIR спектри от две области — 3800–3200  $\text{cm}^{-1}$  и 1500–850  $\text{cm}^{-1}$  са съгласувани с данните от електронно-сондов микроанализ и с петроложките наблюдения. Резултатите показват връзка между тънката структура на спектралните ивици в посочените области и P–T условията на метаморфизма в трите района. Вариациите в ширината и интензивността на основната ивица в OH-областта на ставролитите от района на

Бяла река най-вероятно се дължи на образуване на минерала в интервала на изотермална декомпресия, докато ниската интензивност и малките вариации на тази ивица в ставролитите от Огражден планина показват образуване на минерала в по-тесен температурен интервал. Особеностите в ИЧ-спектъра в диапазона 1500–850  $\text{cm}^{-1}$  могат да се свържат с хетеровалентния Al  $\rightarrow$  Si изоморфизъм в T1 позицията и могат да се обвържат с относително по-високо налягане на образуване на ставролитите от района на Бяла река спрямо тези от Огражден планина.