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# Zn-rich pyroxenes from the ore occurrences in the mixed series in the upper part of the Babuna River, Macedonia

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**Abstract**

The basic purpose of this report was the determination of very fine-grained (cca 0.02-0.05 mm) corroded Zn-rich pyroxenes relics that occur in the mineralized dolomite marbles and baryte schists.

The determination was performed particularly by means of the electron micro-probe analysis that established the new mineral varieties of Zn-rich aegirine-augite composition. The examined pyroxenes were confirmed as pyroxenes, and established by X-ray powder data inside of a complex polyphase mineral system consisting of Zn-rich pyroxenes, Zn-rich richterite, Zn-rich phologopite and baryte.

## Introduction

According to earlier examinations, quartz-cymrite, baryte-cymrite, hyalophane-cymrite, baryte - Zn-rich richterite - Zn-rich glaucophane - tilasite schists were discovered in the surrounding area of the high alkaline aegirine meta-rhyolite in the frame of the so called mixed series of the upper part of the Babuna River region (J a n č e v, 1975). In this region were discovered next to common (baryte, galena, cleiophane, hematite, pyrite etc.) also very rare minerals (gahnite, piemontite, franklinite by B a r i ć (1960) and B a r i ć and I v a n o v (1960). By J a n č e v (1975, 1984a, b, 1990, 1994) and J a n č e v and B e r m a n e e (1997) were discovered later cymrite, sanbornite, hedyphane, celsiane, Pb-piemontite, hancockite, Mn-rich hancockite or Pb-rich piemontite, hyalophane, tilasite, Sb-rich gahnite, Sb-rich franklinite, Zn-rich richterite, and Zn-rich glaucophane.

## Experimental

The Zn-rich pyroxenes samples were primarily reported macroscopic as discrete discontinuous layers or lenses (the thickness of which was around or less than 1 mm) enclosed in dolomite marbles mineralized with baryte, tilasite, Pb-piemontite etc.

Later, Zn-rich pyroxenes were discovered in baryte-Zn-rich richterite-Zn-rich glaucophane-tilasite schists collected many years ago from different parts and levels of the complex polymetallic ore occurrences. These Zn-rich pyroxene lenses are dark greenish-yellowish coloured and resembling epidote. Besides Zn-rich pyroxene layers or lenses in the aforementioned dolomite marbles and baryte schists, also impregnations and disseminated mineralizations of these minerals were discovered.

Zn-rich pyroxenes samples were examined by microscopic methods in thin sections. These examinations show that Zn-rich pyroxenes associations in the frame of the aforementioned lenses or disseminated mineralizations are very fine-grained (less than 0,05 mm) corroded relics and replacements by the younger hydrothermal minerals representing a real handicap for optical and powder X-ray diffraction examinations (Fig. 2 to Fig. 6). Therefore, the considered Zn-rich pyroxenes were determined by means of the electron micro-probe analysis (performed by S. Korikowski from IGEM - AN in Moscow, Russia, and by H. Stančev from IGG in Sofia, Bulgaria) that furnished the preliminary results which were very important for further examinations.

The chemical composition of the minerals was determined at more points scanning at different randomly selected positions from center to the edge of the grain. Chemical formulas were obtained by standard procedures.

The examined pyroxenes were confirmed also by X-ray powder data in a complex poly-phase mineral system containing pyroxenes, richterite, phlogopite in the frame of the treated fine-grained lenses of the mineralized dolomite marbles.

*Acknowledgement.* I am deeply thankful to my colleagues H. Stančev and S. Korikowski for electron micro-probe analysis of the described minerals from Macedonia.

## Results and discussion

In this report are presented data of the Zn-rich pyroxenes that are peculiar mineral varieties of the Zn-rich aegirine-augite composition.

### Zn-rich aegirine-augite

*Occurrence.* In the frame of discrete greenish-yellowish lenses or layers up to 1 mm in thickness, enclosed in dolomite cipolins, Zn-rich aegirine-augite relics were discovered in form of very fine-grained (0,01-0,05 mm), irregular, fibrous, rounded and corroded grains. Besides of Zn-rich pyroxenes in these cipolins were determined Sb-rich gahnite, Sb-rich franklinite, Zn-rich richterite, Zn-rich phlogopite as well as typical hydrothermal minerals - quartz, albite, dolomite, baryte, tilasite etc.

*X-ray powder data.* The greenish-yellowish lenses were separated of the rock by means of a binocular microscope and then treated by classical X-ray diffractometer procedure (Cu $K_a$ / Ni, 40 kV, 20 mA). In the examined sample (Fig. 1) were determined pyroxenes (d(Å)6,30, 4,38, 3,650, 3,350, 3,161, 2,961 etc.), richterite (d(Å)8,19, 3,350, 3,220, 3,160, 2,961 etc.), phlogopite (d(Å)10,04, 3,350, 3,220, 3,022, 2,613 etc.).

*Chemistry.* In the aforementioned corroded pyroxen relics by means of ten electron micro-probe analyses performed by H. Stančev (samples 1, 2, 4,...10) and S. Korikowski (sample 3) the Zn-rich aegirine-augite varieties were determined as follows (Tab. 1):

Table 1. Chemical composition of Zn-rich aegirine-augite samples (%)

| samples | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 55,38 | 55,76 | 56,81 | 56,84 | 60,29 | 58,02 | 54,66 | 53,88 | 53,72 | 55,12 |
| $Al_2O_3$ | 4,98 | 6,81 | 5,39 | 7,76 | 2,35 | 3,98 | 7,66 | 4,85 | 4,50 | 2,01 |
| $Mn_2O_3$ | 0,18 | 0,24 | 0,70 | 0,45 | 0,34 | 0,59 | 0,77 | - | - | - |
| $Fe_2O_3$ | 21,54 | 15,96 | 9,62 | 14,84 | 12,81 | 8,60 | 10,38 | 10,07 | 18,88 | 13,62 |
| CaO | 5,95 | 7,10 | 1,30 | 5,19 | 2,37 | 2,94 | 1,98 | 4,33 | 7,37 | 1,61 |
| MgO | 3,51 | 4,71 | 11,96 | 4,75 | 10,93 | 13,08 | 11,13 | 13,07 | 4,30 | 11,36 |
| ZnO | 0,49 | 0,85 | 5,86 | 0,44 | 4,06 | 4,34 | 5,45 | 5,18 | 1,57 | 8,03 |
| $Na_2O$ | 7,82 | 7,62 | 7,40 | 9,42 | 9,20 | 7,56 | 7,24 | 8,58 | 9,51 | 7,70 |
| PbO | - | - | - | - | - | - | - | - | - | 0,24 |
| Total: | 99,85 | 99,05 | 99,04 | 99,69 | 99,35 | 99,11 | 99,27 | 99,96 | 99,85 | 99,69 |

Remark: total Fe as $Fe_2O_3$

Formulas:

(1)

$$(Na_{0,56}Ca_{0,23}Mg_{0,19}Zn_{0,01})_{0,99}(Fe_{0,59}Al_{0,22}Si_{0,10}Mn_{0,05})_{0,96}Si_{1,93}O_6$$

(4)

$$(Na_{0,66}Mg_{0,25}Ca_{0,05}Zn_{0,01})_{0,97}(Fe_{0,40}Al_{0,33}Ca_{0,15}Si_{0,10}Mn_{0,01})_{0,99}Si_{1,95}O_6$$

(7)

$$(Na_{0,51}Mg_{0,34}Zn_{0,15})_{1,0}(Al_{0,33}Fe_{0,28}Mg_{0,26}Ca_{0,10}Mn_{0,02})_{0,99}Si_{1,99}O_6$$

(10)

$$(Na_{0,56}Mg_{0,22}Zn_{0,22})_{1,0}(Mg_{0,41}Fe_{0,38}Al_{0,1}Ca_{0,06})_{0,95}Si_{2,05}O_6$$

The examined Zn-rich aegirine-augite samples show an evident and very strong linear correlation between MgO and ZnO contents. So, in the aegirine-augite samples containing more than 10% MgO a maximum of 4-8 % ZnO was reported, while samples with less MgO contents (0,35-5,5 % MgO) show 0,44-0,85 % ZnO.

Examined samples No. 3, No. 5 to No. 8 and No. 10 (with cca 4-8 % ZnO respectively) could be considered as peculiar and probably new mineral varieties - Zn-rich aegirine-augite inside of the aegirine-augite series vis á vis the Zn-rich schefferite (with 3,31-3,38 % ZnO) and jeffersonite (with 7,14-10,15 % ZnO), (P a l a c h e, 1960).

## Genesis

The aforementioned Zn-rich pyroxenes determined as Zn-rich aegirine-augite were discovered in mineralized dolomite marbles in forms of fine-grained (cca 0,01-0,05 mm) relics very intensively replaced by younger hydrothermal minerals (baryte, quartz, tilasite etc.) and consequently considered as a contact-metasomatic product that originated at highest temperatures immediately after spinels of gahnite-franklinite type from the post-magmatic oversaturated fluids.

## Conclusions

In dolomite marbles and baryte Zn-rich richterite-tilasite schists from a mixed series in the Precambrian complex of the Pelagonian massif in the upper part of the Babuna river, Macedonia, were discovered the Zn-rich pyroxenes as follows:

- Zn-rich aegirine-augite containing cca 0,5-0,8% ZnO, and
- Zn-rich aegirine-augite with cca 4 - 8% ZnO as a peculiar mineral variety inside the aegirine-augite series.

The aforementioned Zn-rich pyroxenes are considered as typical contact-metasomatic products originated by the action of oversaturated post-magmatic fluids in dolomite marbles and baryte-Zn-rich richterite-tilasite schists.

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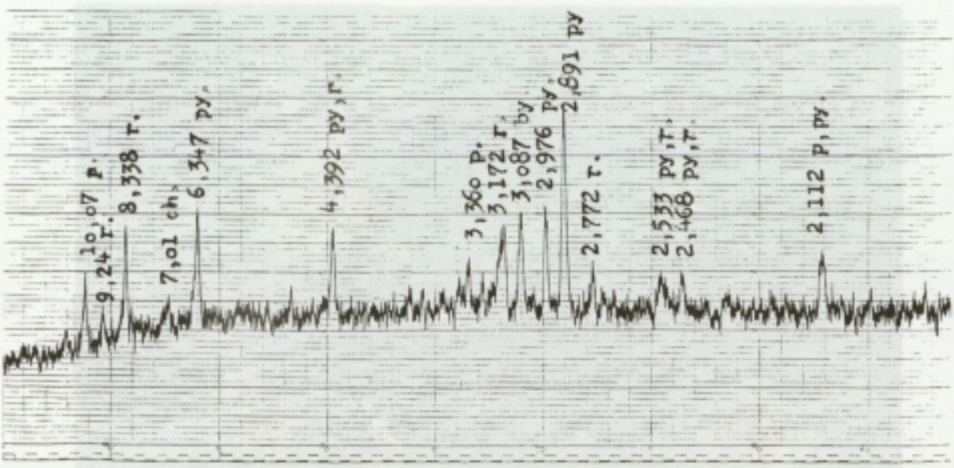


Fig. 1. X-ray powder diagram of Zn-rich aegirine-augite (py) associated with Zn-rich richterite (r.), Zn-rich phlogopite (p.), baryte (by.), chlorite (ch) in the frame of a veinlet enclosed in the mineralized dolomite marbles

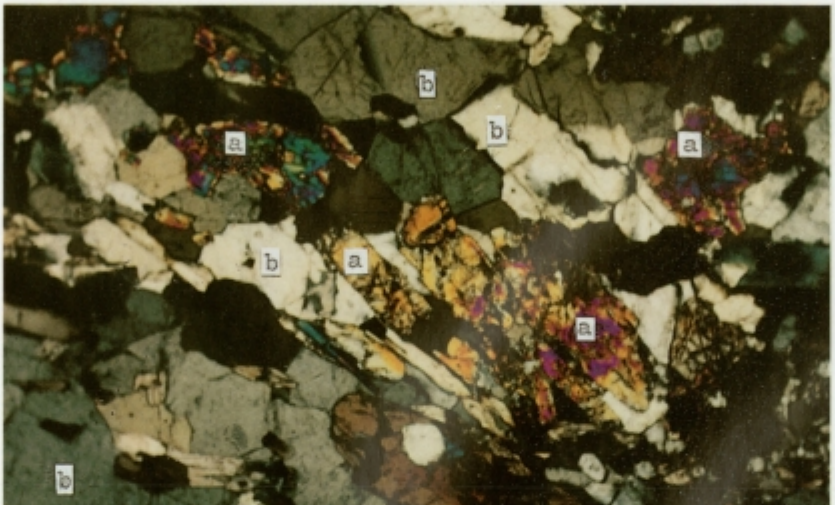


Fig. 2. Corroded and replaced Zn-rich aegirine-augite (a) relics by baryte (b) in baryte schists (N+, photo: S. Jančev)

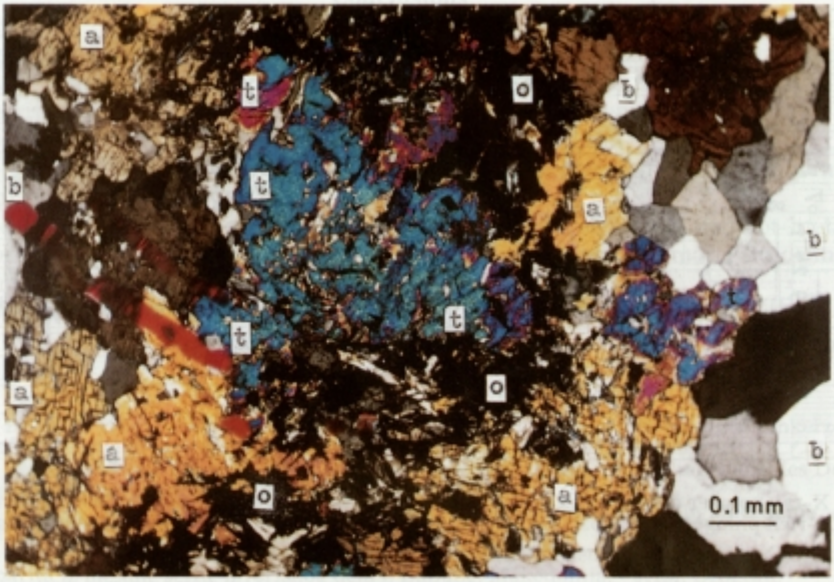


Fig. 3. An association of Zn-rich aegirine-augite (a), tilasite (t), ore minerals (o) inside of a tilasite veinlet enclosed in baryte (b) schist (N+, photo: S. Jančev)

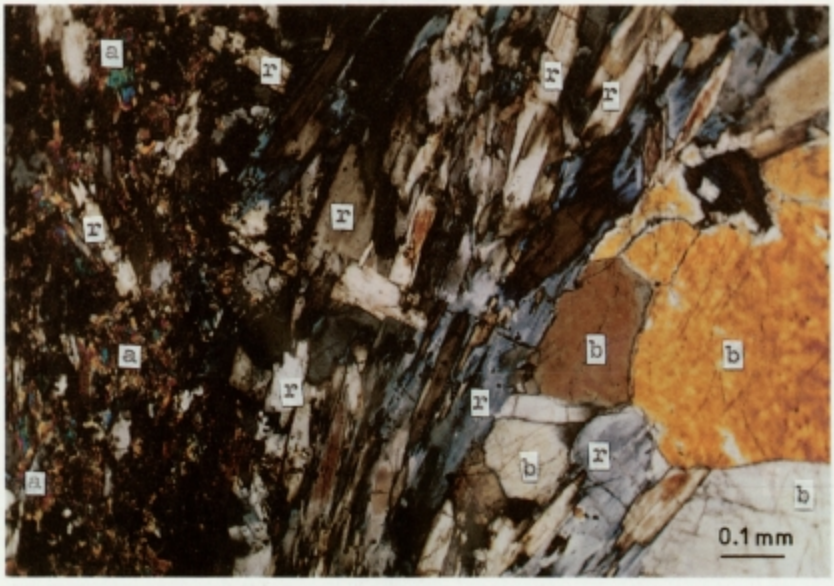


Fig. 4. An association of Zn-rich aegirine-augite (a) and Zn-rich richterite (r) enclosed in baryte (b) schist (N+, photo: S. Jančev)


Fig. 5. Replacements of Zn-rich aegirine-augite (a) by Zn-rich richterite (r) inside of baryte (b) schist (N+, photo: S. Jančev)

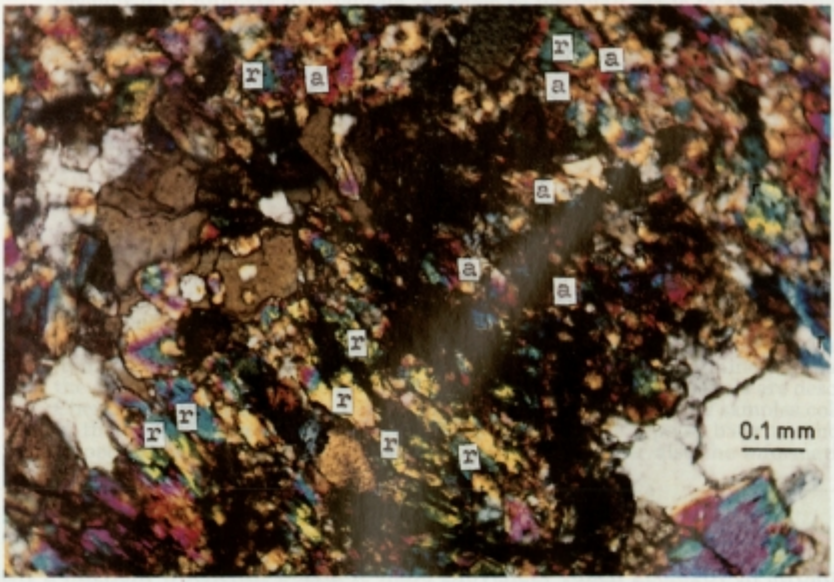


Fig. 6. Super fine-grained associations of Zn-rich aegirine-augite (a) replaced by Zn-rich richterite (r) fibres enclosed in dolomite marble (N+, photo: S. Jančev)