



## Crystal chemistry of clinopyroxene with a high content of the Ca-Tschermak and esseneite components, Eastern Rhodopes, Bulgaria

### Кристалохимия на клинопироксен с високо съдържание на Са-Тс и есенеитов компонент, Източни Родопи, България

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#### Introduction

Esseneite with ideal formula ( $\text{CaFe}^{3+}\text{AlSiO}_6$ ) is silica undersaturated Ca-clinopyroxene with high proportion of Al in the tetrahedral site of the crystal structure. The mineral has been determined by Cosca and Peacor (1987) and was approved as a valid species by the CNMMN, IMA, in 1985. Esseneite is also important component in the chemical composition of subsilicic aluminian ferrian diopside (known in the literature as “fassaite”) – analyses No2 and 3 of eight “unusual pyroxenes”, which were reported by Morimoto et al. (1988).

The major objective of the present work is to provide a crystal chemistry analysis of subsilicic aluminian ferrian diopside, which was found in skarns at Zvezdel-Pcheloyad Pb-Zn deposit. This paper also presents *in situ* LA-ICP-MS data of rare earth and some trace elements for the studied clinopyroxene.

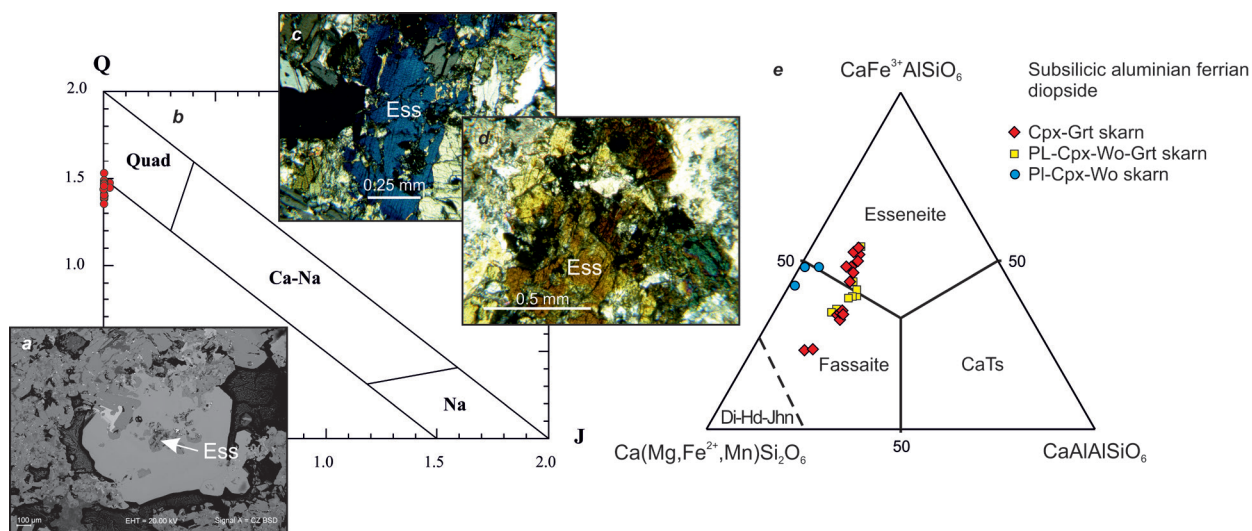
#### Analytical methods

Major elements were analyzed on a ZEISS EVO 25LS scanning electron microscope equipped with an EDAX Trident system at 16 kV accelerating voltage, about 1 nA beam current, using reference standards. After a preliminary petrographic and electron microprobe examination representative samples were chosen for REE and trace element analyses by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). All measurements were carried out on a PerkinElmer ELAN DRC-e ICP-MS instrument integrated with New Wave Research (ESI) UP-193FX ArF excimer laser-ablation system (LA).

#### Results and discussion

Clinopyroxene with a high content of the Ca-Tschermak and esseneite components occurs in skarn xenoliths (nodules), which are hosted by monzonitic rocks of the second intrusive phase of the Zvezdel pluton (Nedialkov, Mavroudchiev, 1995). It is observed in association with melilite ( $\text{Gh}_{62.5-33.5}$ ,  $\text{Ak}_{40.6-22.9}$ ,  $\text{Na-Mll}_{16.3-4.0}$ ,  $\text{Fe-Ak}_{10.9-0.1}$ ,  $\text{Na-Fe}^{3+}\text{-Mll}_{10.3-0.0}$ ), wollastonite-2M, garnets of the grossular-andradite series ( $\text{Adr}_{96.61-3.10}$ ), Ti-rich garnet ( $\text{TiO}_2$  content of 8.04–13.10 wt%), clinopyroxene of the diopside-hedenbergite series ( $\text{Di}_{91.17-27.12}$ ), plagioclase ( $\text{Ab}_{100-3.30}$ ), epidote, prehnite, calcite, quartz, chlorite, thaumasite and zeolites. Titanite, apatite and magnetite are present as accessory minerals. Clinopyroxene commonly occurs as inclusions in garnet poikiloblasts (Fig. 1a) with wollastonite-2M and melilite or as isolated crystals in a quartz-calcite matrix, which exhibit strongly corroded margins. Optically, it shows quite distinctive pleochroism from yellow-green to brown-green, strong dispersion of the optic axes,  $r > v$ , and displays anomalous blue and brown interference colours (Fig. 1c, d).

The chemical composition of the studied clinopyroxene is characterized by significant deficiency of  $\text{SiO}_2$  33.35–39.77 wt% (Si 1.32–1.50 apfu),  $\text{Al}_2\text{O}_3$  ranging from 11.39 to 17.75 wt%, FeO(t) concentrations between 9.67–16.40 wt% ( $\text{Fe}^{3+}$  – 0.180–0.487 apfu), CaO 25.70–23.44 wt%, MgO 4.29–8.37 wt%,  $\text{TiO}_2$  0.7–2.7 wt%, and small amounts of  $\text{Cr}_2\text{O}_3$ , MnO,  $\text{V}_2\text{O}_5$ , and  $\text{Na}_2\text{O}$ . The calculated numbers of Ca, Mg,  $\text{Fe}^{2+}$ , and Na (on the basis of six oxygens) in the M sites (M1 and M2) are plotted in the Q–J diagram (Fig. 1b). Due to the high content of Al and  $\text{Fe}^{3+}$ , and the significant de-



**Fig. 1.** *a*, back-scattered electron image of subsilicic aluminian ferrian diopside (esseneite) in garnet matrix (polished section); *b*, Q–J diagram for clinopyroxenes with Q value less than 1.62 per formula unit; *c–d*, anomalous blue and brown interference colours (under crossed polarized transmitted light); *e*, compositions of the studied clinopyroxenes projected in the system  $\text{Ca(Mg,Fe}^{2+},\text{Mn)Si}_2\text{O}_6$ – $\text{CaAlAlSiO}_6$ – $\text{CaFe}^{3+}\text{AlSiO}_6$  (according to Cosca, Peacor, 1987, modified by Pascal et al., 2005)

iciency of Si atoms, all our compositions appear close to or less than 1.5 Q value, which correspond to the composition of subsilicic aluminian ferrian diopside from the group of “unusual pyroxenes” (according to Morimoto et al., 1988). The end-member compositions are demonstrated on the triangular diagram in terms of the components diopside-hedenbergite-johannsenite ( $\text{Ca(Mg,Fe}^{2+},\text{Mn)Si}_2\text{O}_6$ ), esseneite ( $\text{CaFe}^{3+}\text{AlSiO}_6$ ) and Ca-Tschemak ( $\text{CaAlAlSiO}_6$ ). This projection (Cosca, Peacor, 1987) shows the fields corresponding to dominant cation in the M1 site. All the investigated clinopyroxenes fall in the fields of fassaita and esseneite (Fig. 1e). As shown, a significant part of them would qualify as esseneite (43.5–53.8 mol.% esseneite component).

Trace elements of the analysed clinopyroxenes have been normalized to unaltered monzonitic rock, in order to compare the mobility of these elements during skarn process. The clinopyroxenes are enriched in Ti (0.7–2.7 wt%), Zr (324–530 ppm), Hf (8–12 ppm), V (239–313 ppm), Sc (30–64 ppm), Co (24–28 ppm), Ni (20–32 ppm), and Sn (4–9 ppm). All samples are extremely depleted in LIL elements, Pb, U, and Cu. Slight depletion is observed of REE, Nb, Ta, and Th. The  $\Sigma\text{REE}$  content ranges from 77.95 to 92.74 ppm and is similar to that in the skarn rocks. The chondrite normalized REE patterns exhibit predominance of LREE over HREE with  $\text{La}_N/\text{Yb}_N$  ratio from 4.26 to 10.43 and negative Eu anomaly ( $\text{Eu}/\text{Eu}^* = 0.59$ – $0.78$ ). These observations suggest a relative mobility of Zr, Hf, Ti,

V, Sc, Co, and Ni during the earliest high temperature stage of the skarn process. Their concentration is controlled by the similarity in ionic radii between these elements and major cation in the octahedral sites of the clinopyroxene crystal structure.

The conditions of formation of such rocks, containing subsilicic aluminian ferrian diopside, melilite and wollastonite, are estimated to be at least about 800 °C and a low pressure of  $\text{CO}_2$  (e.g. Jamtveit et al., 1997; Pascal et al., 2005).

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