

Chemical and Mineralogical Characteristics of the Microscopic-sized Epidotes in the Metamorphic Basement Rocks within the Late Cretaceous Hatip Ophiolitic Melange in Konya (Central Southern Turkey)

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ABSTRACT

At the base of the Neotethyan ophiolitic melange, widespread epidote crystals formed in metamorphic rocks of the metamorphic basement, which were experienced a regional metamorphism in green-schist facies conditions. The epidote crystals is subhedral to euhedral, with high Al_2O_3 (26-30 %) and low Fe_2O_3 (5-8%) contents. It is predominantly zoisite ($X_{cz} = 0.46$ to 0.72) and subordinate epidote ($X_{ep} = 0.27-0.53$) in composition, with typical compositional zoning due to variable substitution of Fe^{3+} and Al^{3+} on octahedral sites and sector-zoning. The epidote is suggested to have a possible igneous origin, and to be crystallised from a wet ($H_2O > 5$ wt %) magma under low fO_2 and intermediate pressure conditions during initial stage crystallisation on the basis of its petrographical and mineralogical characteristics.

Keywords:

Epidote; Mineralogy; Chemical zoning; Ophiolite; Konya.

INTRODUCTION

The term epidote $\{Ca_2 Fe_x Al_{3-x} Si_3 O_{12} (OH)\}$ first used in 1801 by Haüy [1], typically forms as a result of medium-temperature alterations of intermediate-basic rocks [2]. However, It is also recognised in various magmatic rocks, e.g. alkaline granite [3], granodiorite, monzogranite [4], tonalite [5], orbicular diorite [6] [7], gabbro [8] and dacite [9]. Epidote can also be developed in eclogites [10], and high-pressure migmatites and pegmatites derived from eclogites [11] [12].

In the SW part of Konya city, widespread epidote minerals occur in the metamorphic basement at the base of Neotethyan ophiolitic melange, which tectonically overlies the Middle Triassic–Upper Cretaceous carbonates (Midostepe and Lorasdağı formations) of the Tauride platform [13] (Fig. 1). The Melange contains Carboniferous-Late Cretaceous carbonates, radiolarian cherts, ultramafic rocks, volcanics and gabbro bodies within sedimentary and sheared serpentinite matrix. Çayırbağı ophiolites obducted onto the melange, and contain various ultramafic rocks, namely, harzburgite, dunite, pyroxenite and gabbro. Substantial magnesite deposits are hosted by serpentinitized harzburgite. The

basement includes various amphibole-bearing metamorphic rocks, namely, amphibolite, epidote-amphibolite, zoisite-amphibolite, garnet-amphibole schist, amphibole schist, plagioclase amphibole schist, plagioclase-epidote-amphibole schist and q-amphibole schist [14]. The contact between the metamorphic basement and the overlying peridotite is represented by 2–3-m-thick, strongly sheared serpentinite and amphibolite schist, with concordant foliation patterns [15]. The metamorphic rocks were subjected to a regional metamorphism in greenschist facies conditions, with development of chlorite and albite crystals. It is aimed to characterize epidote minerals in Ep- amphibolite and zoisite amphibolite using its mineral chemistry.

ANALYTICAL METHODS

From the selected samples, fifty thin sections of were made at thin section laboratory of Department of Geological Engineering (Selçuk University, Konya), and then, their composition and texture were studied under the microscope. Modal mineralogy was determined by point counting (2000-3000 points per thin section, depending on grain size). Chemical

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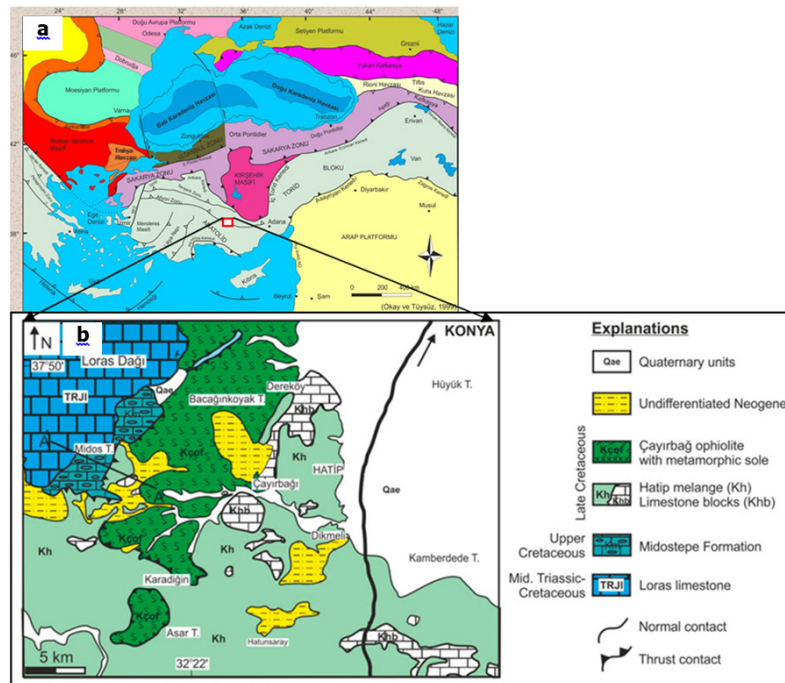


Figure 1. a) Tectonic units of Turkey [16] b) Geological map of the study area [13].

composition of the epidote was determined by electron microprobe at METU, Ankara (Turkey). Operating conditions were kept at an accelerating voltage of 15 kV and a beam current of 20 nA. A beam size of 5 μm was used on amphibole and biotite grains, whereas a defocused beam of 10 μm was used on plagioclase grains to limit Na loss.

PETROGRAPHY

The epidote amphibolite consists of amphibole (0.6 mm, 65.3%), epidote (0.1-0.4 mm 23.47 %), zoisite (0.1-0.3 mm,

5%), plagioclase (5.5 %), quartz (0.7%) and titanite (0.03%) in a granular texture. The amphiboles exhibits typical light and yellowish green colour and pleochroism, and are magnesiohornblende, pargasite and edenite in composition [14]. The epidotes mostly forms as single grain or rarely in aggregate, which is subhedral to euhedral (Fig. 2a), with high (II and III order) birefringence colour. It develops mostly colour-zoned isometric or stubby prismatic (Fig. 2 a, b); the cores are pale yellowish-green and pleochroic, but the rims are nearly colourless. Though it is not common, sector-zoning is also observed in the

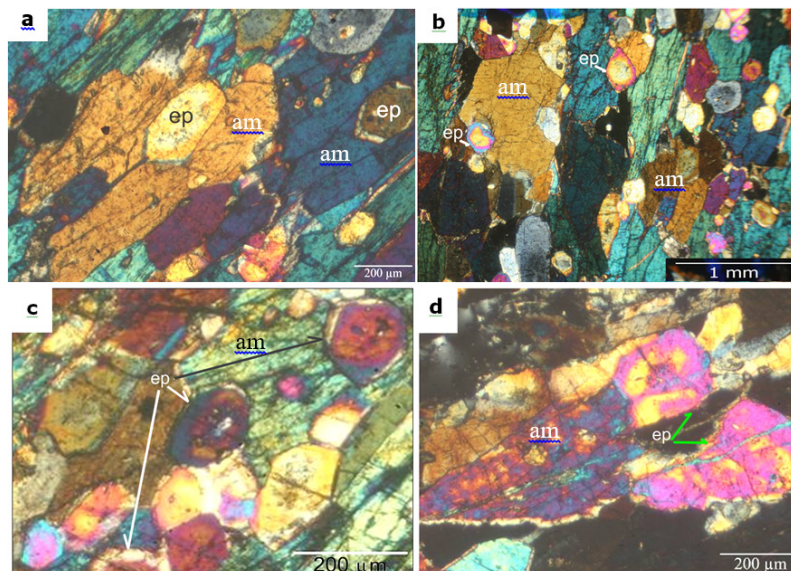


Figure 2. Microphotograph of the epidote amphibolite, ep: epidote, am: amphibole; a) Euhedral epidote (ep) growth within the amphibole, b) epidote replacing the subhedral amphibole. c-d) sector-zoning in the epidote. Cross-Nicholls(XN)

samples (Fig. 2 c, d). The plagioclase is altered to calcite and sericite.

The zoisite amphibolite is composed of amphibole (52.2 %), zoisite (38.4 %), plagioclase (0.5 mm, 7.1 %) and titanite (2.3 %) in a granular texture. The amphibole (0.3-0.7 mm) is predominantly subhedral, and exhibits greenish colour and pleochroism, and resorbed by epidote crystals (Fig. 2a, b). Zoisite (0.3 mm) occurs as aligned anhedral crystals, with low birefringence colour. The titanite (0.4 mm) forms as rhomboeder crystals, and exhibit brownish colour due to its FeO content.

MINERAL CHEMISTRY

Chemical compositions of the epidotes are presented in Table 1, which has limited compositional range of pistacite [$XPs = Fe^{3+}/(Fe^{3+} + Al) \times 100$] of 7% and 16% Fig. 3), and of $CaO = 23.4-25.5$ wt%. The epidote minerals contain minor amounts of TiO_2 (0.05 to 0.31, with an average of 0.18 wt %), MnO (0.01 to 0.17 wt %) and MgO (0.0 to 0.4, with an average of 0.12 wt%). But they are distinguished from typical epidotes [2] with higher contents of Al_2O_3 (26-30 against 20.32%) and lower contents of Fe_2O_3 (5-8

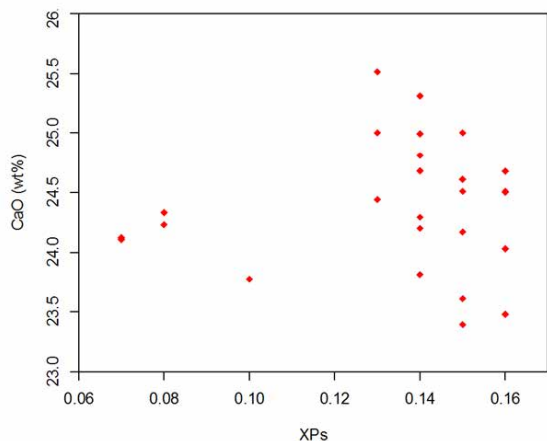


Figure 3. X Ps-CaO (wt%) relationship of epidote minerals in metabasic rocks.

Table 1. Chemical analyses of the epidote minerals, the formula is normalized on Si = 3 apfu due to high Si value ($Si > 3.05$ apfu, [18]).

| Wt% | G ₃ -1-3 | G ₃ -1-7 | G ₃ -1-8 | G ₃ -2-Z1-1 | G ₃ -3-8 | G ₃ -3-9 | M-1-2 | M-1-3 | M-1-6 | M-1-9 | M-1-2-1 | M-1-2-2 | M-1-2-5 |
|--------------------------------|---------------------|---------------------|---------------------|------------------------|---------------------|---------------------|-------|-------|-------|-------|---------|---------|---------|
| SiO ₂ | 39.12 | 39.24 | 39.22 | 39.24 | 39.35 | 39.37 | 38.35 | 38.86 | 38.43 | 39.36 | 38.42 | 38.73 | 37.58 |
| TiO ₂ | 0.16 | 0.14 | 0.14 | 0.15 | 0.18 | 0.12 | 0.18 | 0.16 | 0.23 | 0.17 | 0.28 | 0.18 | 0.09 |
| Al ₂ O ₃ | 27.25 | 27.49 | 27.54 | 27.24 | 27.10 | 26.97 | 27.84 | 26.57 | 27.93 | 27.46 | 28.04 | 27.69 | 27.68 |
| Cr ₂ O ₃ | 0.04 | 0.11 | 0.11 | 0.05 | 0.00 | 0.02 | 0.08 | 0.22 | 0.08 | 0.05 | 0.17 | 0.20 | 0.02 |
| Fe ₂ O ₃ | 7.23 | 6.68 | 6.68 | 7.43 | 7.64 | 7.75 | 6.66 | 7.89 | 6.32 | 6.84 | 7.06 | 6.77 | 7.61 |
| MnO | 0.07 | 0.09 | 0.09 | 0.14 | 0.12 | 0.14 | 0.07 | 0.01 | 0.03 | 0.08 | 0.09 | 0.11 | 0.14 |
| MgO | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.11 | 0.10 | 0.17 | 0.12 | 0.11 | 0.01 | 0.12 |

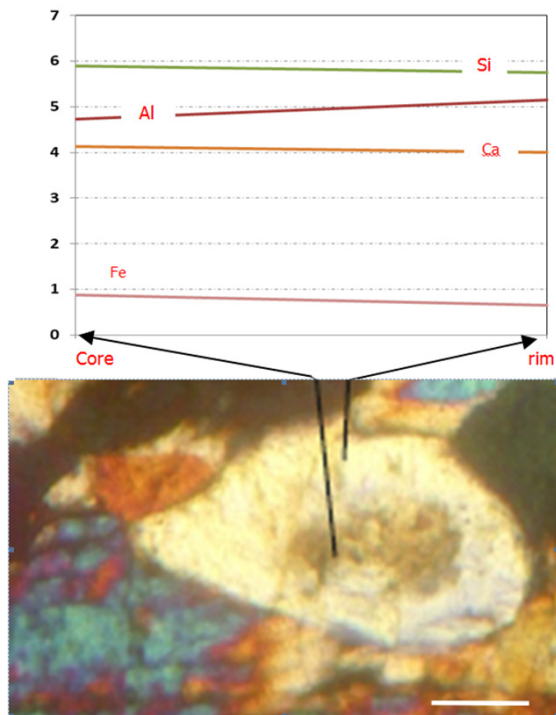


Figure 4. Chemical zoning of the epidote. Scale bars represent 0.03 mm

against 17.75%).

In thin section, the zoning is occasionally clear from the colour variation/intensity, nonetheless characteristically shows up in the interference colours, in that birefringence is a strong function of the chemical composition, especially the Fe-Al content. Single epidote grains commonly exhibits a growth zoning; the core shows relative enrichment in Fe, Si and Ca, and depletion in Al in comparing with its rim (Fig. 4). Based on the molar fractions of the end-members, it has been classified in the epidote solid solutions series as epidote and zoisite; they were calculated respectively as: $XFe^{3+} = Fe^{3+} / (Fe^{3+} + Al^{3+} - 2 + Cr^{3+})$, $XAl^{3+} = (Al^{3+} - 2) / (Fe^{3+} + Al^{3+} - 2 + Cr^{3+})$ [17]. The epidote crystals are mostly zoisite (Xcz) in composition, ranging from $Xcz = 0.46-0.72$ (Table 1), while epidote composition (Xep) also exists, with $Xep = 0.27-0.53$.

Table 1. Chemical analyses of the epidote minerals, the formula is normalized on Si = 3 apfu due to high Si value (Si > 3.05 apfu, [18]) (cont.).

| Wt% | G ₃₋₁₋₃ | G ₃₋₁₋₇ | G ₃₋₁₋₈ | G _{3-2- z1-1} | G ₃₋₃₋₈ | G ₃₋₃₋₉ | M-1-2 | M-1-3 | M-1-6 | M-1-9 | M-1- 2-1 | M-1- 2-2 | M-1- 2-5 |
|--|--------------------|--------------------|--------------------|----------------------------|--------------------|--------------------|----------------|----------------|-------------|--------------|--------------|-------------------|-------------------|
| CaO | 24.23 | 24.11 | 24.12 | 24.33 | 23.39 | 24.03 | 25.00 | 24.50 | 25.51 | 24.20 | 24.29 | 24.68 | 25.00 |
| Na ₂ O | 0.01 | 0.00 | 0.00 | 0.02 | 0.00 | 0.04 | 0.07 | 0.02 | 0.01 | 0.11 | 0.02 | 0.00 | 0.04 |
| TOTAL | 98.11 | 97.86 | 97.89 | 98.59 | 97.78 | 98.44 | 98.35 | 98.33 | 98.71 | 98.38 | 98.47 | 98.36 | 98.28 |
| <i>Based on 8 cations and 12.5 oxygens</i> | | | | | | | | | | | | | |
| Si | 3.03 | 3.04 | 3.04 | 3.04 | 3.05 | 3.05 | 2.97 | 3.01 | 2.98 | 3.05 | 2.98 | 3.00 | 2.91 |
| Ti | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 |
| Al | 2.49 | 2.51 | 2.51 | 2.49 | 2.47 | 2.46 | 2.54 | 2.43 | 2.55 | 2.51 | 2.56 | 2.53 | 2.53 |
| Cr | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 |
| Fe ₂ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Fe ₃ | 0.21 | 0.19 | 0.19 | 0.22 | 0.45 | 0.45 | 0.39 | 0.46 | 0.37 | 0.40 | 0.41 | 0.39 | 0.44 |
| Mn ₃₊ | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 |
| Mg | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.00 | 0.01 |
| Ca | 2.01 | 2.00 | 2.00 | 2.02 | 1.94 | 1.99 | 2.07 | 2.03 | 2.12 | 2.01 | 2.02 | 2.05 | 2.07 |
| Sr | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Na | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.01 |
| XFe ₃₊ | 0.30 | 0.27 | 0.27 | 0.31 | 0.48 | 0.49 | 0.42 | 0.51 | 0.40 | 0.44 | 0.42 | 0.42 | 0.46 |
| XAl ₃₊ | 0.70 | 0.72 | 0.72 | 0.69 | 0.52 | 0.50 | 0.58 | 0.47 | 0.60 | 0.56 | 0.57 | 0.56 | 0.54 |
| XPs | 0.08 | 0.07 | 0.07 | 0.08 | 0.15 | 0.16 | 0.13 | 0.16 | 0.13 | 0.14 | 0.14 | 0.14 | 0.15 |
| Wt% | M-1- 3-1 | M1- 4-a2 | M1- 4-e2 | M1-4- pl1-1 | M1-4- pl1-2 | M1-4- pl1-3 | M1-4- pl1-5 | M1-4- pl1-7 | M1- 4-z1 | M4- tüm-5 | M4- tüm-6 | M4- tüm2- 1 | M4- tüm2- 7 |
| SiO ₂ | 38.85 | 39.31 | 39.01 | 38.13 | 37.69 | 39.23 | 38.17 | 39.15 | 39.30 | 38.47 | 39.19 | 39.28 | 37.91 |
| TiO ₂ | 0.19 | 0.22 | 0.05 | 0.20 | 0.20 | 0.20 | 0.16 | 0.16 | 0.15 | 0.31 | 0.17 | 0.25 | 0.15 |
| Al ₂ O ₃ | 27.03 | 26.14 | 27.23 | 27.36 | 27.36 | 27.36 | 27.52 | 26.58 | 26.51 | 27.20 | 29.83 | 26.85 | 27.76 |
| Cr ₂ O ₃ | 0.08 | 0.04 | 0.10 | 0.10 | 0.10 | 0.10 | 0.09 | 0.09 | 0.14 | 0.07 | 0.06 | 0.14 | 0.04 |
| Fe ₂ O ₃ | 6.76 | 7.61 | 7.26 | 7.15 | 7.15 | 7.15 | 7.60 | 7.67 | 7.20 | 7.57 | 5.09 | 7.90 | 6.75 |
| MnO | 0.07 | 0.07 | 0.11 | 0.17 | 0.17 | 0.17 | 0.08 | 0.08 | 0.07 | 0.09 | 0.09 | 0.05 | 0.12 |
| MgO | 0.16 | 0.19 | 0.14 | 0.14 | 0.14 | 0.14 | 0.08 | 0.08 | 0.14 | 0.30 | 0.18 | 0.22 | 0.40 |
| CaO | 24.99 | 24.68 | 23.61 | 24.81 | 25.31 | 23.81 | 24.51 | 24.51 | 24.61 | 24.17 | 23.77 | 23.48 | 24.44 |
| Na ₂ O | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.04 | 0.02 | 0.09 | 0.08 | 0.02 | 0.15 |
| TOTAL | 98.19 | 98.24 | 97.50 | 98.07 | 98.13 | 98.17 | 98.24 | 98.35 | 98.16 | 98.27 | 98.46 | 98.20 | 97.72 |
| <i>Based on 8 cations and 12.5 oxygens</i> | | | | | | | | | | | | | |
| Si | 3.01 | 3.05 | 3.02 | 2.95 | 2.92 | 3.04 | 2.96 | 3.03 | 3.04 | 2.98 | 3.04 | 3.04 | 2.94 |
| Ti | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 |
| Al | 2.47 | 2.39 | 2.49 | 2.50 | 2.50 | 2.50 | 2.51 | 2.43 | 2.42 | 2.48 | 2.72 | 2.45 | 2.53 |
| Cr | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 |
| Fe ₂ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

Table 1. Chemical analyses of the epidote minerals, the formula is normalized on Si = 3 apfu due to high Si value (Si > 3.05 apfu, [18]) (cont.).

| Wt% | M-1-3-1 | M1-4-a2 | M1-4-e2 | M1-4-pl1-1 | M1-4-pl1-2 | M1-4-pl1-3 | M1-4-pl1-5 | M1-4-pl1-7 | M1-4-z1 | M4-tüm-5 | M4-tüm-6 | M4-tüm2-1 | M4-tüm2-7 |
|-------------------|---------|---------|---------|------------|------------|------------|------------|------------|---------|----------|----------|-----------|-----------|
| Fe ₃ | 0.39 | 0.44 | 0.42 | 0.42 | 0.42 | 0.42 | 0.44 | 0.45 | 0.42 | 0.44 | 0.30 | 0.46 | 0.39 |
| Mn | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 |
| Mg | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 | 0.02 | 0.03 | 0.02 | 0.03 | 0.05 |
| Ca | 2.07 | 2.05 | 1.96 | 2.06 | 2.10 | 1.98 | 2.03 | 2.03 | 2.04 | 2.01 | 1.97 | 1.95 | 2.03 |
| Sr | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Na | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.02 |
| XFe ₃₊ | 0.45 | 0.53 | 0.46 | 0.45 | 0.45 | 0.45 | 0.46 | 0.51 | 0.49 | 0.48 | 0.29 | 0.50 | 0.42 |
| XAl ₃₊ | 0.54 | 0.46 | 0.53 | 0.54 | 0.54 | 0.54 | 0.53 | 0.49 | 0.50 | 0.52 | 0.71 | 0.49 | 0.57 |
| XPs | 0.14 | 0.16 | 0.15 | 0.14 | 0.14 | 0.14 | 0.15 | 0.16 | 0.15 | 0.15 | 0.10 | 0.16 | 0.13 |

$$XAl_{3+} = (Al^{3+} - 2) / (Fe^{3+} + Al^{3+} - 2 + Cr^{3+})$$

$$XFe^{3+} = Fe^{3+} / (Fe^{3+} + Al^{3+} - 2 + Cr^{3+})$$

$$XPs = Fe^{3+} / (Fe^{3+} + Al^{3+})$$

DISCUSSIONS AND CONCLUSION

Pistacite [Ps: Fe³⁺/(Fe³⁺ Al)], and TiO₂ wt % contents of epidote were substantial to determine its origin. In the literature review, Ps ranges in igneous epidotes are as follows; (1) 25-29% [19], (2) 23-27% [20], (3) 19-24% [21], (4) 26-33% [22], (5) 30-70 % [23], (6) 21-26 % [8], (7) 16-29% [24]. [19] suggested that epidotes formed from alteration of plagioclase varied from Ps0 to Ps24 those formed by alteration of biotite varied from Ps36 to Ps48. In sum, Ps content range 16-70, and 0-48 % in igneous and secondary epidotes. [23] also suggest that metamorphic epidotes show pistacite molar percentage of 0 to 100 %. The samples have Ps content varies from Ps7 to Ps16, suggesting both metamorphic and secondary (plagioclase alteration) origin. Secondary epidote is usually smaller in comparing with igneous epidote, and forms as a product of alteration of plagioclase [25]. Generally, the unsaturated nature of plagioclase, with small-intermediate size is unfavour of secondary origin.

[9] suggest that igneous epidote has TiO₂ <0.2 wt%. Similarly [22] reported that igneous and secondary epidotes have TiO₂ contents <0.2 wt% and >0.6 wt (%), respectively. In metamorphic epidote, TiO₂ ranges are as follows; 0.01-0.14% in greenschist metabasite [26], 0.02-0.12 % in epidote blueschist [10], 0.08-0.64 % in garnet amphibolite [27], 0.07 to 0.22 wt% in eclogite and associated metabasite [10], and 2.06 wt% TiO₂ in epidote-glaucophane-blueschist [28]. TiO₂ contents of the samples range from 0.05 to 0.31 wt%, but mostly less than 0.2 wt%, suggesting an igneous origin of the epidotes in the samples.

[20] suggested that igneous epidote may have some textural and phase relationship as follows; (a) epidote overprinting

ehedral allanite, (b) ehedral slightly pleochroic epidote in biotite, (c) embayed hornblende by epidote, (d) wormy intergrowths with plagioclase and/or quartz, (e) epidote associated with magmatic flow banding, and (f) crystallisation of epidote in unaltered rocks. (g) Igneous epidote can also form as inclusion in primary muscovite [29], (h) inclusion in biotite and K-feldspar [30], and (i) exhibit fine scale oscillatory zoning [9]. The epidote is subhedral to ehedral (Fig. 2), and embays and truncates an optically continuous amphibole, confirming an igneous origin for epidote. [31] suggest that the amphibole in the samples may have igneous origin and crystallized under a medium pressure (≤ 7 kb) based on characteristics of their mineral chemistry. The samples is also characterised by the lack of pyroxene crystals possibly due to high content of water in the magma [32] [33]. It was experimentally shown that high H₂O contents, 5wt % at 400MPa, or 7-9 wt % at 960 MPa, may cause amphibole to be the liquidus silicate phase, and impede pyroxene crystallisation [32] [33]. Taking account the extensive crystallisation of amphibole in the samples and its intermediate crystallisation pressure, it is likely that the magma could have water contents higher than 5 wt % during initial stage of crystallization. [34] shows experimentally that Fe³⁺ content of epidote increases with fO₂, and decreasing fO₂ induce epidote more aluminous. Low pistacite content (Ps7-16) of the samples indicates low fO₂ conditions during crystallisation of the magma.

Consequently, petrographical characteristics and mineral chemistry of the epidote in metamafic rocks from metamorphic basement suggests that the epidote crystals are of igneous in origin, and likely to be crystallized from a magma with high water content (higher than 5 wt %) and low fO₂ conditions during initial stage of crystallization.

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