

## Article

# Mineral Chemistry Studies on Pyroxenes in Fe Skarns in the West of Elazığ (Turkey); Their Role in the Skarn Mineralization Process

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## Abstract

This study presents the first detailed investigation of pyroxene zoning within polymetallic skarn zones of the Elazığ region. Skarns develop along contacts between plutonic rocks (diorite and granite) and carbonate rocks, forming two main zones: endoskarn and exoskarn. Endoskarns exhibit clear mineralogical zoning, including pyroxene–garnet, pyroxene–scapolite, and epidote–garnet assemblages, while scapolite occurs in both endoskarn and exoskarn zones. Minor serpentinized olivine within endoskarns is attributed to localized magnesium enrichment due to partial assimilation of low-Mg magma by dolomitic marbles. Geochemical analyses reveal systematic variations in pyroxene composition related to ore type: Cu–Fe skarns show low Mn/Fe ratios (<0.1) and low Zn (~200 ppm), Fe skarns have high Mn/Fe ratios (>0.2) and elevated Zn (>200 ppm), and W-bearing skarns display intermediate Mn/Fe ratios (~0.15) with high Zn (>500 ppm). These findings highlight the value of pyroxene Mn/Fe ratios and Zn contents as indicators of hydrothermal fluid evolution and skarn-forming processes. Overall, this study provides the first evidence of oscillatory zoning in pyroxenes from polymetallic skarns in the region, demonstrating the interplay between magmatic differentiation and hydrothermal mineralization.

**Keywords:** Elazığ magmatites; compositional zoned; pyroxenes; skarn mineral

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## 1. Introduction

The Skarn deposits associated with shallow magmatic systems are among the most common ore deposits typically found within or adjacent to carbonate rocks [1]. Based on their geological settings and contained metals, numerous types have been identified, including Fe, Ti, Cu, Zn, Au, Mo, W, and Sn skarns [2]. Unlike other types of skarn deposits, Zn skarns form in magmatic intrusions that exhibit a wide compositional range, from granite to diorite, and are often located at a considerable distance from the intrusive body. This suggests that skarn formation is more complex than previously assumed and indicates that development of skarns is influenced by various geological factors during the migration of magmatic fluids released from intrusions. Consequently, parameters such as composition of magmatic intrusion, distance to the magmatic body, the ratio of skarn to sulfide minerals, formation temperatures, and morphology of skarn structure contribute to development of distinct skarn-forming mechanisms [2]. Although it is generally argued that fluids involved in skarn formation are of magmatic origin, some researchers [2,3] have presented evidence suggesting increasing fluid input even at considerable distances from magmatic intrusion.

In some cases, skarn formation predominantly occurs through the replacement of carbonate rocks, and such types of mineralization are typically characterized by greater size and ore abundance [4].

Several studies have been conducted on the Elazığ magmatic skarn formation, oxide-sulfide mineralization, the timing of skarn development, and the age of associated magmatic rocks [5–9]. The Southeastern Anatolian Orogenic Belt (SAOB) is a component of the Zagros Mountains of Iran and the Oman-Makran subduction system in Türkiye. Within this area, many skarn formations associated with A-type granitoids have developed due to subduction. [10,11]. The skarn formations within the Elazığ magmatites mostly developed at hot contacts between diorite, tonalite, gabbro rocks, and Keban marbles (Figure 1). Examples of such mineralization include the Pertek and Demürek skarns, Çavuşlu Fe skarns, Birvan, Meşeli and Keban Pb–Zn skarns [6,7,12,13].

In addition to garnet and pyroxene—the two primary minerals of skarn environments—other minerals such as quartz, calcite, humite, epidote, periclase, phlogopite, talc, serpentine, and brucite are also observed. The concept of skarn zoning, first introduced by Meinert [1,2], refers to development of zonation in silicate minerals, which typically forms in areas proximal to intrusive rock and/or fluid-bearing channels within the magmatic intrusion. The distal zone, composed of minerals such as vesuvianite, wollastonite, bustamite, or rhodonite, is where mineral zonation is most clearly observed. The formation of such garnet requires a high concentration of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ . According to Tagirov et al. [4], Al-rich hydrothermal fluids have low solubility, and Fe is typically limited in areas close to intrusive rocks. Therefore, garnet formation associated with skarn-type mineralization is primarily controlled by the availability of  $\text{Fe}^{3+}$  [3,14]. The iron content is also important for pyroxene formation, with redox conditions and the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio being additional key factors. Under conditions where the magma is oxidizing and country rocks are reducing, a garnet > pyroxene zone typically develops in the proximal region, while a pyroxene > garnet zone is more common in the distal region. The relative widths of these zones depend on the degree of oxidation. In contrast, garnet is more abundant than pyroxene in settings where both magma and host rocks are oxidizing [14–16]. Sectoral or oscillatory growth zoning in garnet is characteristic of proximal skarn zones, whereas zoning in pyroxene is rarely observed. In this study, the oscillatory zoning and chemical composition of pyroxene minerals within the skarn zone between the Elazığ magmatites and Keban metamorphics will be used to investigate the role of fluids in silicate mineral zoning, as well as to interpret mineralization evolution and associated physico-chemical conditions (e.g., redox state, pH) during skarn formation.

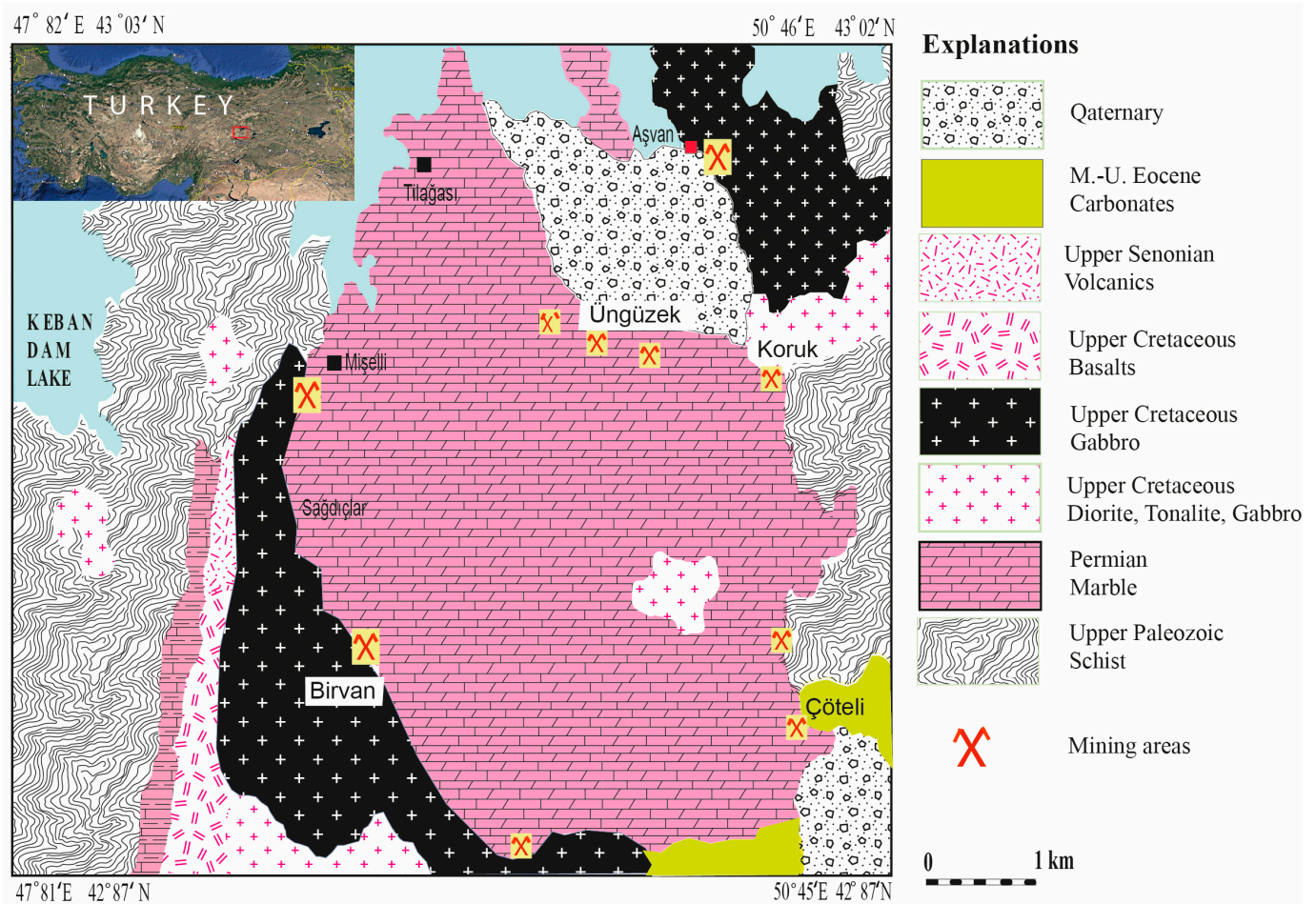


**Figure 1.** Geological map of the study area [17].

## 2. Materials and Methods

Pyroxene samples were collected from the skarn zone between the Keban marbles and Elazığ magmatics in the study area (Figure 1). EPMA were conducted at the Analytical Laboratories of the Department of Geological Engineering, Ankara University (YEBİM). All analytical results are presented in Table 1. BSE imaging and elemental mapping were performed at the Institute of Geology, Bulgarian Academy of Sciences, using a JEOL Superprobe 733 equipped with an ORTEC energy-dispersive detector system, operating at an accelerating voltage of 25 keV. Pure metals and compounds were used as standards, including Ag, Co, Ni, FeS<sub>2</sub>, Sb<sub>2</sub>S<sub>3</sub> (for Sb), CuFeS<sub>2</sub> (for Fe), Cu<sub>3</sub>AsS<sub>4</sub> (for Cu, As, and S), ZnS (for Zn), CdS (for Cd), and HgS (for Hg). SEM analyses along pyroxene and garnet mineral boundaries were carried out at Bartın University Research and Application Center (BAUM), and diagrams illustrating elemental distributions were presented.

**Table 1.** Electron microprobe analyses (EPMA) and LA-ICP-MS analyses of pyroxene in the Elazığ Magmatic Fe skarn.

| Sample No.                         |       | Px-1  |       |       |       |       |       | Px-2 |       |       |       | Px-3  |       |       |       | Px-4 |       |      |      |       |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|------|-------|------|------|-------|
| Position                           | rim   | rim   | core  | core  | rim   | rim   | core  | core | rim   | rim   | rim   | rim   | core  | core  | rim   | rim  | core  | core | rim  | rim   |
| SiO <sub>2</sub>                   | 46.6  | 53.1  | 48.3  | 54.1  | 51.8  | 52.9  | 50.7  | 54.2 | 52.3  | 50.7  | 54.1  | 53.7  | 55.6  | 57.1  | 55.0  | 52.1 | 52.8  | 51.9 | 50.0 | 51.0  |
| Al <sub>2</sub> O <sub>3</sub>     | 8.09  | 3.15  | 6.66  | 0.88  | 4.40  | 2.74  | 3.73  | 2.24 | 5.13  | 5.17  | 1.65  | 2.42  | 0.61  | 0.85  | 1.54  | 3.22 | 2.95  | 2.22 | 4.61 | 5.33  |
| TiO <sub>2</sub>                   | 0.81  | 0.40  | 0.39  | 0.14  | 0.38  | 0.40  | 0.25  | 0.08 | 0.27  | 0.45  | 0.07  | 0.07  | 0.00  | 0.00  | 0.06  | 0.07 | 0.14  | 0.05 | 0.27 | 0.34  |
| FeO                                | 5.69  | 2.45  | 4.57  | 1.11  | 3.67  | 2.12  | 3.55  | 2.67 | 4.04  | 3.19  | 2.09  | 2.47  | 0.67  | 0.68  | 2.16  | 2.84 | 3.36  | 2.14 | 4.35 | 4.59  |
| MgO                                | 13.3  | 16.6  | 13.21 | 18.07 | 15.6  | 16.6  | 15.9  | 16.2 | 14.6  | 14.3  | 17.3  | 16.6  | 17.7  | 17.1  | 16.2  | 16.1 | 16.1  | 16.7 | 15.3 | 14.4  |
| MnO                                | 0.06  | 0.07  | 0.05  | 0.08  | 0.11  | 0.10  | 0.06  | 0.09 | 0.09  | 0.10  | 0.05  | 0.05  | 0.04  | 0.01  | 0.07  | 0.08 | 0.10  | 0.06 | 0.07 | 0.07  |
| CaO                                | 24.6  | 25.0  | 24.7  | 25.3  | 24.8  | 25.2  | 25.0  | 24.9 | 24.7  | 24.8  | 24.8  | 25.3  | 24.7  | 24.4  | 24.9  | 25.1 | 24.9  | 25.4 | 25.3 | 25.2  |
| Na <sub>2</sub> O                  | 0.00  | 0.00  | 0.01  | 0.00  | 0.01  | 0.01  | 0.00  | 0.01 | 0.01  | 0.02  | 0.03  | 0.01  | 0.11  | 0.08  | 0.02  | 0.01 | 0.07  | 0.08 | 0.00 | 0.01  |
| Cr <sub>2</sub> O <sub>3</sub>     | 0.04  | 0.01  | 0.02  | 0.01  | 0.00  | 0.00  | 0.01  | 0.00 | 0.11  | 1.01  | 0.00  | 0.01  | 0.41  | 0.45  | 0.00  | 0.02 | 0.00  | 0.01 | 0.00 | 0.22  |
| Total                              | 102   | 101   | 97.4  | 99.7  | 100   | 100   | 99.3  | 100  | 101   | 99.7  | 99.2  | 100   | 99.8  | 100   | 99.9  | 99.5 | 100   | 98.5 | 99.9 | 101   |
| Number of cations                  |       |       |       |       |       |       |       |      |       |       |       |       |       |       |       |      |       |      |      |       |
| Si                                 | 1.74  | 1.88  | 1.85  | 1.97  | 1.82  | 1.90  | 1.90  | 1.92 | 1.80  | 1.91  | 1.95  | 1.92  | 2.01  | 2.01  | 1.93  | 1.90 | 1.90  | 1.95 | 1.85 | 1.88  |
| Al                                 | 0.29  | 0.14  | 0.24  | 0.03  | 0.17  | 0.13  | 0.18  | 0.11 | 0.21  | 0.21  | 0.97  | 0.12  | 0.03  | 0.02  | 0.05  | 0.13 | 0.11  | 0.07 | 0.21 | 0.22  |
| Ti                                 | 0.02  | 0.01  | 0.01  | 0.00  | 0.01  | 0.01  | 0.01  | 0.00 | 0.01  | 0.01  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00 | 0.00  | 0.00 | 0.01 | 0.01  |
| Fe <sup>2+</sup>                   | 0.18  | 0.08  | 0.14  | 0.04  | 0.11  | 0.07  | 0.11  | 0.08 | 0.13  | 0.09  | 0.05  | 0.06  | 0.01  | 0.01  | 0.08  | 0.09 | 0.09  | 0.10 | 0.11 | 0.16  |
| Fe <sup>3+</sup>                   | 2.86  | 2.96  | 2.80  | 2.84  | 2.90  | 2.82  | 2.83  | 2.85 | 2.86  | 2.88  | 2.88  | 2.89  | 2.90  | 2.87  | 2.91  | 2.83 | 2.81  | 2.82 | 2.84 | 2.77  |
| Mn                                 | 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  | 0.00  | 0.00  | 0.00 | 0.00  | 0.00 | 0.00 | 0.00  |
| Cr                                 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00 | 0.00  | 0.03  | 0.00  | 0.00  | 0.01  | 0.02  | 0.00  | 0.00 | 0.00  | 0.00 | 0.00 | 0.01  |
| K                                  | 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  | 0.00  | 0.00  | 0.00 | 0.00  | 0.00 | 0.00 | 0.00  |
| Mg                                 | 0.71  | 0.90  | 0.79  | 0.96  | 0.85  | 0.90  | 0.88  | 0.87 | 0.81  | 0.78  | 0.93  | 0.89  | 0.96  | 0.91  | 0.88  | 0.87 | 0.84  | 0.91 | 0.84 | 0.75  |
| Ca                                 | 0.95  | 0.94  | 0.95  | 0.97  | 0.97  | 0.96  | 0.97  | 0.95 | 0.95  | 0.96  | 0.94  | 0.96  | 0.96  | 0.95  | 0.96  | 0.96 | 0.91  | 1.00 | 1.01 | 0.98  |
| Fe <sup>3+</sup> /Fe <sup>2+</sup> | 16    | 37    | 20    | 71    | 26    | 40    | 26    | 36   | 22    | 32    | 58    | 48    | 290   | 287   | 36    | 31   | 31    | 28   | 26   | 17    |
| Trace elements (ppm)               |       |       |       |       |       |       |       |      |       |       |       |       |       |       |       |      |       |      |      |       |
| Ba                                 | 0.19  | 0.13  | 0.22  | 1.01  | 0.20  | 0.51  | 0.15  | 1.02 | 0.15  | 0.11  | 0.11  | 0.23  | 0.21  | 0.88  | 0.49  | 0.35 | 0.34  | 0.90 | 0.17 | 0.31  |
| Rb                                 | 0.07  | 0.08  | 0.05  | 0.09  | 0.10  | 0.08  | 0.09  | 0.14 | 0.16  | 0.13  | 0.11  | 0.07  | 0.06  | 0.13  | 0.11  | 0.04 | 0.03  | 0.08 | 0.14 | 0.06  |
| Cs                                 | 0.01  | 0.02  | 0.02  | 0.03  | 0.04  | 0.01  | 0.01  | 0.04 | 0.02  | 0.35  | 0.03  | 0.01  | 0.02  | 0.06  | 0.02  | 0.03 | 0.01  | 0.03 | 0.02 | 0.02  |
| V                                  | 7.52  | 10.7  | 7.59  | 5.00  | 7.30  | 5.44  | 9.97  | 6.10 | 6.52  | 6.88  | 5.77  | 4.79  | 6.54  | 8.02  | 11.1  | 6.60 | 10.1  | 10.5 | 5.78 | 9.92  |
| Co                                 | 0.84  | 0.85  | 0.92  | 0.90  | 0.90  | 0.84  | 1.51  | 1.59 | 0.89  | 1.22  | 0.84  | 0.90  | 1.56  | 1.45  | 0.88  | 0.69 | 1.31  | 1.37 | 1.08 | 0.94  |
| Sr                                 | 19.0  | 20.6  | 15.2  | 20.1  | 15.5  | 15.9  | 18.3  | 19.7 | 22.3  | 15.3  | 15.1  | 15.1  | 16.1  | 15.1  | 16.1  | 17.1 | 20.5  | 22.6 | 20.3 | 18.2  |
| Th                                 | 0.04  | 0.02  | 0.04  | 0.03  | 0.02  | 0.06  | 0.07  | 0.31 | 0.02  | 0.14  | 0.02  | 0.01  | 0.01  | 0.01  | 0.07  | 0.01 | 0.01  | 0.01 | 0.03 | 0.03  |
| U                                  | 0.01  | 0.01  | 0.01  | 0.00  | 0.02  | 0.01  | 0.16  | 0.08 | 0.01  | 0.04  | 0.01  | 0.02  | 0.06  | 0.09  | 0.02  | 0.02 | 0.06  | 0.01 | 0.02 | 0.09  |
| Y                                  | 0.64  | 0.90  | 0.17  | 0.18  | 0.91  | 1.58  | 0.17  | 0.17 | 0.29  | 1.28  | 0.13  | 0.29  | 0.78  | 0.45  | 1.20  | 0.27 | 0.30  | 0.14 | 0.11 | 0.37  |
| Cu                                 | 3.11  | 2.57  | 2.60  | 2.51  | 2.60  | 3.01  | 2.33  | 2.77 | 2.94  | 2.56  | 3.02  | 3.01  | 2.39  | 2.50  | 2.82  | 2.91 | 3.08  | 3.15 | 3.17 | 2.72  |
| Zn                                 | 216   | 233   | 227   | 229   | 239   | 233   | 221   | 215  | 219   | 221   | 222   | 241   | 215   | 225   | 211   | 218  | 220   | 220  | 233  | 225   |
| Pb                                 | 0.69  | 0.78  | 0.33  | 0.39  | 0.40  | 1.12  | 0.54  | 1.01 | 0.29  | 0.30  | 0.36  | 0.31  | 0.60  | 0.78  | 0.35  | 0.23 | 0.48  | 1.25 | 0.29 | 1.02  |
| Mo                                 | 6.70  | 6.51  | 5.97  | 6.59  | 6.11  | 6.19  | 5.49  | 5.41 | 6.88  | 6.60  | 6.50  | 6.91  | 5.90  | 6.00  | 7.01  | 6.50 | 7.23  | 5.85 | 6.58 | 5.70  |
| Ga                                 | 1.22  | 1.20  | 1.39  | 1.60  | 1.45  | 1.32  | 1.40  | 1.25 | 0.60  | 0.70  | 0.66  | 0.59  | 1.30  | 1.82  | 0.75  | 0.70 | 1.74  | 1.78 | 1.50 | 1.63  |
| Ag                                 | 0.02  | 0.03  | 0.03  | 0.04  | 0.03  | 0.04  | 0.05  | 0.06 | 0.07  | 0.07  | 0.07  | 0.06  | 0.04  | 0.05  | 0.04  | 0.06 | 0.05  | 0.05 | 0.06 | 0.04  |
| LILE                               | 20.0  | 21.6  | 15.9  | 21.7  | 16.3  | 17.7  | 19.3  | 22.0 | 22.9  | 16.4  | 15.74 | 15.73 | 17.1  | 17.0  | 17.2  | 17.8 | 21.4  | 24.9 | 21.0 | 19.6  |
| Sr/Y                               | 29.68 | 22.88 | 89.41 | 111.6 | 17.03 | 10.06 | 107.6 | 116  | 79.89 | 11.95 | 116   | 52.06 | 20.64 | 33.55 | 13.41 | 63.3 | 68.33 | 161  | 185  | 49.18 |

Table 1. Cont.

| Sample No.                       |      | Px-1                      |      |       |      |       |       |       | Px-2 |      |      |      | Px-3 |      |      |      | Px-4  |       |      |      |  |
|----------------------------------|------|---------------------------|------|-------|------|-------|-------|-------|------|------|------|------|------|------|------|------|-------|-------|------|------|--|
|                                  |      | Rare earth elements (ppm) |      |       |      |       |       |       |      |      |      |      |      |      |      |      |       |       |      |      |  |
| La                               | 0.03 | 0.02                      | 0.06 | 0.11  | 0.14 | 0.17  | 0.12  | 0.30  | 0.12 | 0.22 | 0.52 | 0.68 | 0.78 | 0.35 | 0.39 | 0.61 | 0.54  | 0.65  | 0.05 | 0.06 |  |
| Ce                               | 1.34 | 1.29                      | 1.34 | 3.10  | 1.80 | 2.52  | 1.65  | 4.39  | 1.10 | 1.34 | 1.14 | 1.12 | 5.69 | 4.20 | 1.10 | 1.11 | 1.63  | 4.39  | 4.45 | 5.88 |  |
| Pr                               | 0.03 | 0.03                      | 0.03 | 0.34  | 0.22 | 0.21  | 0.18  | 0.67  | 0.02 | 0.07 | 0.02 | 0.01 | 0.66 | 0.57 | 0.03 | 0.02 | 0.17  | 0.40  | 0.41 | 0.89 |  |
| Sm                               | 0.02 | 0.07                      | 0.05 | 0.19  | 0.20 | 0.18  | 0.13  | 0.34  | 0.06 | 0.14 | 0.08 | 0.08 | 0.67 | 0.75 | 0.07 | 0.10 | 0.10  | 0.14  | 0.25 | 0.51 |  |
| Nd                               | 0.59 | 0.07                      | 0.02 | 0.11  | 0.19 | 0.20  | 0.17  | 0.95  | 0.30 | 0.21 | 0.30 | 0.17 | 0.89 | 0.30 | 0.90 | 0.41 | 0.77  | 0.24  | 0.36 | 0.85 |  |
| Eu                               | 0.05 | 0.02                      | 0.02 | 0.07  | 0.03 | 0.06  | 0.02  | 0.05  | 0.02 | 0.03 | 0.02 | 0.01 | 0.04 | 0.05 | 0.03 | 0.02 | 0.03  | 0.09  | 0.07 | 0.10 |  |
| Dy                               | 0.06 | 0.11                      | 0.06 | 0.04  | 0.11 | 0.20  | 0.07  | 0.06  | 0.05 | 0.22 | 0.03 | 0.10 | 0.20 | 0.31 | 0.70 | 0.38 | 0.06  | 0.04  | 0.07 | 0.09 |  |
| Tb                               | 0.02 | 0.02                      | 0.03 | 0.02  | 0.02 | 0.05  | 0.02  | 0.02  | 0.02 | 0.03 | 0.01 | 0.01 | 0.07 | 0.12 | 0.03 | 0.03 | 0.02  | 0.02  | 0.01 | 0.03 |  |
| Gd                               | 0.10 | 0.10                      | 0.16 | 0.10  | 0.12 | 0.19  | 0.09  | 0.17  | 0.04 | 0.19 | 0.06 | 0.07 | 0.59 | 0.60 | 0.09 | 0.11 | 0.09  | 0.14  | 0.20 | 0.31 |  |
| Ho                               | 0.03 | 0.03                      | 0.01 | 0.01  | 0.05 | 0.05  | 0.01  | 0.01  | 0.01 | 0.05 | 0.01 | 0.01 | 0.03 | 0.14 | 0.25 | 0.11 | 0.01  | 0.01  | 0.01 | 0.01 |  |
| Tm                               | 0.01 | 0.01                      | 0.02 | 0.01  | 0.02 | 0.02  | 0.01  | 0.01  | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.04 | 0.12 | 0.05 | 0.01  | 0.01  | 0.01 | 0.01 |  |
| Er                               | 0.05 | 0.06                      | 0.05 | 0.02  | 0.10 | 0.20  | 0.03  | 0.02  | 0.05 | 0.11 | 0.02 | 0.02 | 0.07 | 0.02 | 0.19 | 0.01 | 0.02  | 0.03  | 0.02 | 0.04 |  |
| Yb                               | 0.03 | 0.07                      | 0.07 | 0.03  | 0.13 | 0.16  | 0.04  | 0.05  | 0.04 | 0.12 | 0.02 | 0.04 | 0.10 | 0.14 | 0.11 | 0.15 | 0.04  | 0.03  | 0.02 | 0.03 |  |
| Lu                               | 0.03 | 0.01                      | 0.01 | 0.01  | 0.02 | 0.03  | 0.01  | 0.01  | 0.01 | 0.02 | 0.03 | 0.01 | 0.01 | 0.03 | 0.14 | 0.03 | 0.01  | 0.01  | 0.01 | 0.02 |  |
| ΣREE                             | 2.39 | 1.91                      | 1.93 | 4.16  | 3.15 | 4.24  | 2.55  | 7.05  | 1.85 | 2.76 | 2.27 | 2.34 | 9.81 | 7.26 | 4.42 | 3.14 | 3.50  | 6.16  | 5.94 | 8.83 |  |
| ΣLREE                            | 2.06 | 1.51                      | 1.52 | 3.92  | 2.58 | 3.34  | 2.27  | 6.70  | 1.62 | 2.01 | 2.08 | 2.07 | 8.73 | 6.22 | 2.52 | 2.27 | 3.24  | 5.91  | 5.59 | 8.29 |  |
| ΣHREE                            | 0.33 | 0.40                      | 0.41 | 0.24  | 0.57 | 0.90  | 0.28  | 0.35  | 0.23 | 0.75 | 0.19 | 0.27 | 1.08 | 1.04 | 1.90 | 0.87 | 0.26  | 0.25  | 0.35 | 0.54 |  |
| LREE/HREE                        | 6.24 | 3.77                      | 3.70 | 16.3  | 4.52 | 3.71  | 8.10  | 19.14 | 7.04 | 2.68 | 10.9 | 7.66 | 8.08 | 5.98 | 1.32 | 2.60 | 12.46 | 23.6  | 15.9 | 15.3 |  |
| La <sub>N</sub> /Yb <sub>N</sub> | 0.66 | 0.18                      | 0.55 | 2.62  | 0.70 | 0.62  | 2.13  | 4.40  | 1.87 | 1.40 | 16.1 | 11.5 | 0.51 | 1.51 | 2.54 | 2.86 | 7.87  | 12.09 | 1.14 | 1.56 |  |
| Eu/Eu*                           | 1.94 | 0.67                      | 0.37 | 1.36  | 0.46 | 0.91  | 0.59  | 0.75  | 1.09 | 0.42 | 0.61 | 0.56 | 0.19 | 0.18 | 0.75 | 0.47 | 0.99  | 1.87  | 1.04 | 0.82 |  |
| Ce/Ce*                           | 8.51 | 11.24                     | 5.67 | 3.70  | 2.39 | 2.37  | 2.60  | 2.37  | 5.22 | 2.71 | 2.03 | 2.49 | 5.93 | 2.36 | 2.61 | 2.00 | 1.46  | 2.16  | 7.89 | 5.53 |  |
| Diopside                         | 99.7 | 99.6                      | 99.5 | 100.0 | 99.7 | 100.0 | 100.0 | 99.9  | 99.8 | 99.8 | 99.7 | 99.7 | 99.3 | 99.5 | 99.8 | 99.8 | 99.5  | 99.4  | 99.9 | 99.9 |  |

$$\text{Eu/Eu}^* = \text{Eu}_N / (\text{Sm}_N \times \text{Gd}_N)^{1/2}, \text{Ce/Ce}^* = \text{Ce}_N / (\text{La}_N \times \text{Pr}_N)^{1/2}.$$

### 3. Results

#### 3.1. Geology

The Keban metamorphics exhibit extensive outcrops around Birvan village and outcrop in a narrow area around Aşvan. The unit is represented by marble and calcphyllite lithologies around Birvan and consists of marbles around Aşvan. While the marbles are coarser-grained at the contact with Elazığ magmatites, they become finer-grained as they move away from the contact. In the Late Cretaceous, the Keban metamorphics exhibited metamorphism between the greenschist facies and amphibolite facies due to the arc magmatism that formed the Elazığ magmatites [6]. Initially described by Özgül [18] as part of the Carboniferous–Triassic-aged Alanya unit, subsequent studies have revealed similarities between the Keban unit and the Aladağ unit [18] and Bolkar Mountains unit [19], which range in age from the Late Devonian to Late Cretaceous. Supporting evidence includes the absence of metamorphism in the Aladağ unit, leading to the recognition of the Keban metamorphics as a metamorphic equivalent of the Bolkar Mountains unit [19,20].

The regionally metamorphosed Keban metamorphics consist, from the lower to upper levels, of recrystallized limestone, calcschist, carbonate metaclastic rocks, and carbonate rocks (dolomitic/recrystallized limestone). At the base of metamorphic unit, a chlorite–sericite phyllite/schist level predominates. Above this, metaconglomerate, calcphyllite, and graphite schist levels are present. The Permian–Lower Triassic metamorphic unit underwent metamorphism during the Upper Cretaceous [20]. Asutay [21] suggested that the protolith of the Keban metamorphics was carbonate sandstone.

The Elazığ magmatites represent a Late Cretaceous–Paleocene magmatic body that intrudes the Keban metamorphics [6,20,21]. This A-type magmatic body is derived from a crustal source modified by subduction processes. The Elazığ magmatites consist of plutonic rocks such as gabbro, diorite, monzonite, tonalite, and granite, along with their equivalent surface and subaerial rocks around Elazığ. The unit consists of gabbro-diorite, tonalite, and basalts around Birvan and Aşvan, and gabbro-diorite around Aşvan. It has been suggested that gabbros, diorite, tonalite, and basalts are products of arc magmatism and granites are products of collision [21–24].

#### 3.2. Mineralisation

Late Cretaceous–Paleocene-aged diorite, granodiorite, tonalite, and gabbro intrude the Keban metamorphics, forming the metasomatic skarn zone associated with local injections (Figure 2). This zone hosts a Fe-Ti skarn mineralization and has a width ranging from 0.5 to 3.0 m [5,6,9,12,13]. The narrow endoskarn zone consists of grossular garnet (Grt 1), iron-rich grossular (Grt 2), and andradite (Grt 3), together with diopside and plagioclase. The exoskarn is composed of grossular (Grt 4), pyroxene, and vesuvianite. Ore minerals include magnetite, hematite, ilmenite, pyrite, galena, sphalerite, and chalcopyrite.

The mineral paragenesis of the Keban metamorphics comprises garnet, pyroxene (diopside), plagioclase, scolecite, quartz, calcite, muscovite, and chlorite. The diopside–vesuvianite–grossular–wollastonite mineral assemblage indicates hornblende–hornfels facies metamorphic conditions of approximately 530 °C at 1000 bar and 540 °C at 2000 bar [25]. The mineral chemistry of garnets suggests that Grt 1 precipitated under low water-to-rock (W/R) ratios and relatively reduced conditions. Oscillatory zoning observed in silicate minerals is attributed to infiltration metasomatism associated with high Fe<sup>3+</sup> concentrations and elevated W/R ratios. When water–rock interactions decrease, residual Al-bearing metasomatic fluids derived from calcschist under reducing conditions influence zoning patterns.



**Figure 2.** (a,b) Lithological units in studied area, (c) calcsilicate rocks in Keban metamorphics, (d) carbonates of Keban metamorphics and Elazığ magmatites.

Oxide and sulfide mineralization within the skarn zone likely formed immediately following alteration of primary anhydrous calc-silicate minerals. At this stage, iron mineralization developed alongside actinolite, epidote, quartz, and occasionally tremolite. The presence of magnetite between garnet crystals indicates that this mineral precipitated after primary skarn formation.

Zoning in silicate minerals within skarn deposits provides insights into crystal growth processes and environment in which crystals developed. The oscillatory-zoned pyroxene is fine- to medium-grained and subhedral in shape. Microscopic examinations identified it as diopside, with an extinction angle of approximately 40 degrees. Diopside is closely associated with garnet and occurs in irregular aggregates (Figure 1). Oscillatory zoning in pyroxenes results from chemical variations and ion exchanges within hydrothermal fluid. The hydrothermal process promotes regular nucleation of minerals, manifesting as oscillatory zoning (Figure 3b,d). The predominance of diopside in analyzed pyroxenes indicates that the early-stage skarn-forming hydrothermal fluids were generally under

high oxygen fugacity conditions, consistent with previous studies [25,26] and supported by measured  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios ( $\sim 59$ ). Because, in a high oxygen fugacity ( $f\text{O}_2$ ) environment, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio is generally considered to be above 0.5,  $\text{Fe}^{3+}$  is more dominant than  $\text{Fe}^{2+}$ . The composition of analyzed pyroxenes being predominantly diopside indicates that hydrothermal fluids responsible for mineralization during early skarn stages were generally under high oxygen fugacity conditions [26]. Magnetite, ilmenite, hematite, chalcopyrite, pyrite, along with quartz, and calcite developed during the retrograde phase [27]. Garnet, one of primary minerals of skarn formation, exhibits euhedral morphology. Hand specimens commonly display garnets with a color range from dark green to light green and from light brown to dark brown. In regions with intense iron precipitation, garnets are dark brown, whereas those near carbonates are green. This color variation is attributed to diversity of cations transported by hydrothermal fluids [28,29]. Garnet crystal sizes range from approximately 0.3 to 1 cm. According to Plumlee et al. [30], garnet crystal size depends on flow rate of hydrothermal fluid and degree of chemical equilibrium between fluid and host rock. In thin sections, most garnet crystals have weathered extensively and turned into secondary minerals (Figure 3).

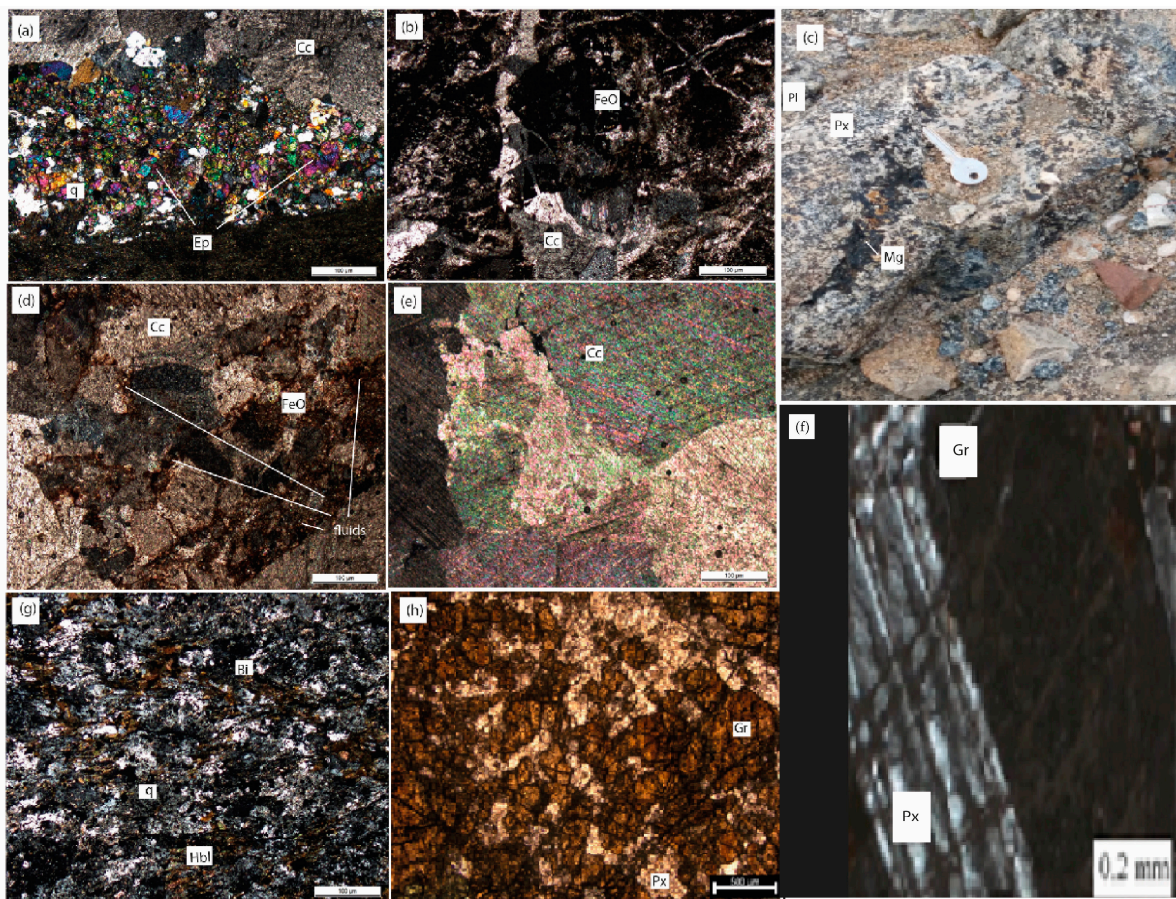


**Figure 3.** Macroscopic and microscopic images of garnet (Gr) and clinopyroxene (Px) minerals. (a) Skarn zone containing calcite (Cc), epidote (Ep), quartz (q), and opaque minerals (FeO); (b) skarn zone with FeO, quartz (q), and calcite (Cc); (c) macroscopic appearance of clinopyroxenes; (d) brown-colored brecciated carbonate rock altered by Fe-rich solutions; (e) white marble with phenocrysts; (f) microscopic image of the pyroxene analyzed by SEM and EPMA; (g) schist belonging to the Keban metamorphics containing quartz (q), biotite (Bt), and magnetite (Mg); (h) microscopic view of diopside (Px) and garnet (Gr).

### 3.3. Zoning

The physicochemical conditions (P, T), fluid composition, redox state, and fugacity during crystallization in pyroxenes of the skarn zone induce oscillatory zoning [31,32]. This oscillatory zoning develops as a result of thermal and chemical diffusion processes during crystal growth and is particularly influenced by factors such as repeated fluid transport along fractures in hydrothermal system [33] or multiple effects of magmatic fluids [34]. The limited diffusion rates of cations within silicate minerals are believed to drive development of oscillatory zoning, which serves as an important record providing insights into mineral growth history and controlling processes of skarn formation [35,36].

Figure 3 presents images of the skarn zone, displaying garnet and pyroxene minerals in both a hand specimen and under a polarizing microscope. It is observed that clinopyroxenes reach sizes exceeding 1.5 cm in macroscopic samples. The oscillatory zoning observed in BSE and X-ray dot map images reflects the diopside composition (Figure 4). The crystal core exhibits a less hedenbergitic composition, while the mantle is predominantly diopside (Table 1). The outermost rim displays oscillatory zoning. These images demonstrate rhythmic compositional variations from core to rim in pyroxene crystals. The presence of redox conditions, which have been reported to influence zoning development in various studies [36,37], is corroborated by the  $\text{Fe}^{3+}$  content in mineralization. This further supports that the garnet/pyroxene ratio is especially dependent on the ferric/ferrous iron ratio.

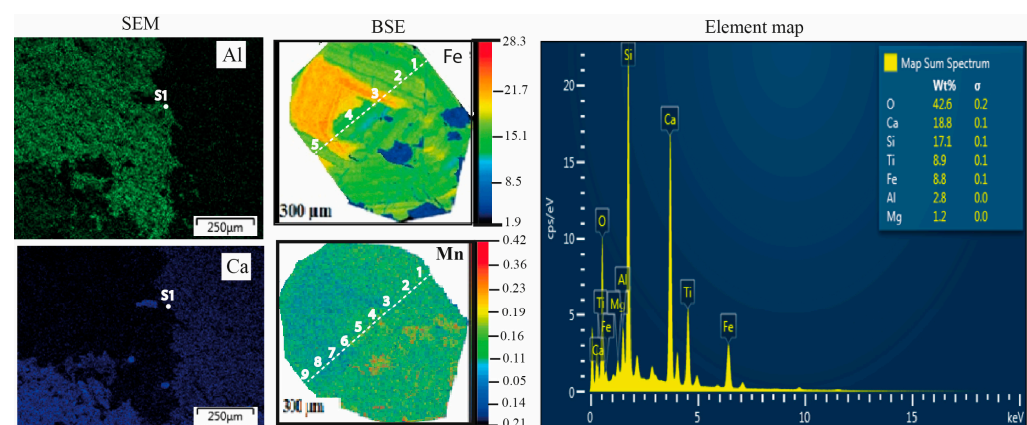


**Figure 4.** SEM and EPMA element map of zoned pyroxene. Color scales in parts per million.

The calcium–silicate skarnization in western Elazığ is characterized by the presence of garnet, pyroxene, scapolite, and calcite. The distribution of these mineral assemblages and their spatial relationship to contact zone allow skarn to be distinctly divided into two main zones: endoskarn and exoskarn. The endoskarn zone is relatively narrow, whereas exoskarn zone is more extensive. Within this area, minerals such as magnetite, hematite, pyrite, quartz, epidote, garnet, biotite, and tremolite-actinolite are commonly observed. Endoskarns develop at contacts between dioritic and granitic plutonic rocks and marbles, as well as within the intrusive body itself. Endoskarns at diorite–carbonate contacts are particularly prevalent around Birvan, Mişelli, Üngüzek, Çötel, Koruk, and Aşvan (Figure 1), while endoskarns at granite–carbonate contacts are predominant outside the study area, particularly in northern Elazığ, around Pertek, Demürek, and Meşeli. The endoskarn zone exhibits mineralogical zoning characterized by pyroxene–garnet, pyroxene–scapolite, and epidote–garnet assemblages. Scapolite group minerals, commonly occurring as euhedral, prismatic, or tabular crystals, are present in both endoskarn and exoskarn zones. Although olivine is absent in dioritic host rocks, the presence of minor serpentinized olivine crystals within endoskarn zone is attributed to localized magnesium enrichment resulting from partial assimilation of magma with low Mg content by dolomitic marbles [37].

In the exoskarn zone, calcite, dolomite, and minor amounts of quartz predominate. Closer to the magmatic body, minerals such as garnet, scapolite, pyroxene-epidote, titanite, and magnetite are observed. While titanite is not found within carbonate rocks, well-developed crystals occur within exoskarn zones. In his study, Öztunalı [38] states that the Keban skarn zone is the most important polymetallic ore deposit in the Eastern Anatolia Region.

The alteration types observed in region include silicification (e.g., chert and opal), which largely depends on composition of host rocks. According to Plumlee [30], silica precipitation may indicate dilution and cooling of ore-bearing fluids through mixing with other fluids. Silica-rich magmatic, hydrothermal, or metamorphic fluids tend to deposit silica under favorable conditions such as decreases in pressure, temperature, or solution pH. Slow cooling of hydrothermal solutions results in quartz crystallization. Silicification can occur through two primary mechanisms: (1) the addition of silica to rock by hydrothermal or magmatic solutions and (2) the relative enrichment of silica caused by dissolution of other minerals in rock. Iron oxide alteration, which includes minerals such as hematite, is typically associated with quartz and chlorite. The presence of these minerals suggests that iron necessary for formation of iron-bearing ores was transported by hydrothermal fluids and precipitated under favorable physicochemical conditions. Carbonatization (e.g., dolomitization) involves formation of dolomite, sericite, and quartz, and is commonly observed in limestones under low to moderate temperature conditions. Another important alteration type in the Elazığ Fe skarn deposit is decarbonization. This alteration results from interaction of carbonate- or  $\text{HCO}_3^-$ -rich fluids with host rocks. It is particularly common in sedimentary rocks, where these fluids dissolve existing carbonates, leading to formation of secondary calcite and a subsequent pH shift in adjacent non-carbonate rocks.

### 3.4. Geochemistry

The results of EPMA (Electron Probe Micro-Analysis), presented in Table 1, indicate that the pyroxenes exhibit compositional zoning between their darker and lighter domains. The pyroxenes, identified as having a diopside composition, display well-developed zoning in backscattered electron images (Figure 4). In these BSE images, chemical variations defined by differences in Mn and Fe referred to as growth zoning (Figure 4) may exhibit regional variations depending on associated metal assemblages, despite the relatively consistent contents of Fe, Mn, and Zn in pyroxenes. In the SEM-BSE images (Figure 4), variations in Al and Ca within the same mineral are clearly observed. The Ca enrichment peaks in elemental maps indicate a diopside composition of pyroxene. The brighter tones in BSE images correspond to areas with higher concentrations of Ca, an element with a higher atomic number. This observation is consistent with microscopic textures and EPMA analytical results, confirming that the pyroxene in the sample crystallized with a Ca–Mg-rich diopside composition.

From a silica perspective, pyroxene cores are richer in  $\text{SiO}_2$  (53.1 wt%) compared to their rims (51.46 wt%). The cores also contain  $\text{MgO}$  (16.0 wt%), while  $\text{FeO}$  (2.42 wt%),  $\text{TiO}_2$  (0.14 wt%),  $\text{CaO}$  (24.91 wt%), and  $\text{MnO}$  (0.07 wt%) are present in lower concentrations. The contents of other oxides remain nearly constant throughout the crystal. EPMA data in Table 1 indicate that pyroxene crystals are predominantly composed of diopside. Similarly, the Mg–Fe–Ca ternary diagram based on EPMA data confirms that the pyroxene composition corresponds to diopside (Figure 5). A strong positive correlation between Fe and Al contents is observed, suggesting that Fe and Al do not coexist in solid solution, consistent with previous findings [27]. The high  $\text{SiO}_2$  content implies limited silica mobility within host rock, whereas elevated concentrations of Ca, Al, and Mg indicate influence of metasomatic processes on mineral chemistry and mineralization. The relatively low

MgO content may reflect partial assimilation of dolomitic marbles by shoshonite magma. The reduced CaO concentrations may indicate incorporation of calcium into plagioclase, scapolite, garnet, and calcite mineral structures.

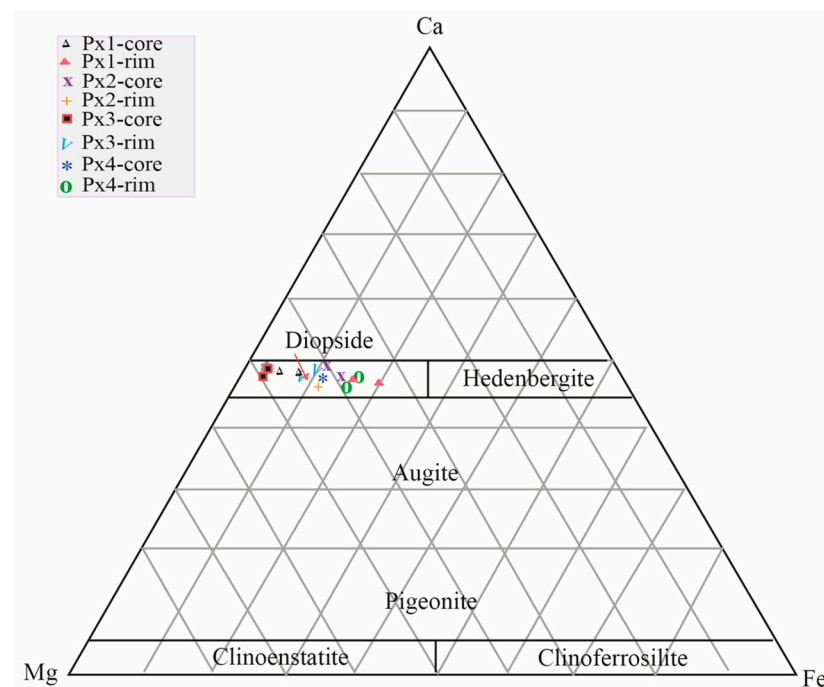


**Figure 5.** Pyroxene chemical composition diagram [34].

Pyroxenes from skarns hosting copper-iron (Cu-Fe) mineralization are typically characterized by a low Mn/Fe ratio ( $<0.1$ ) and low Zn content (approximately 200 ppm). In contrast, those associated with Fe mineralization exhibit a high Mn/Fe ratio ( $>0.2$ ) and elevated Zn content ( $>200$  ppm). Pyroxenes from tungsten (W)-bearing skarn zones generally show an intermediate Mn/Fe ratio ( $\sim 0.15$ ) and a high Zn content ( $>500$  ppm) [30]. The systematic relationship between pyroxene composition and ore type reflects relative proportions of Mn, Fe, Zn, and Cd in hydrothermal fluids from time of pyroxene formation through to subsequent sulfide precipitation. Accordingly, Zn content and Mn/Fe ratio of skarn pyroxenes are valuable indicators for classifying and characterizing skarn-forming environments. These classification criteria are consistent with observations from the study area, where the Mn/Fe ratio is  $<0.1$  and Zn content exceeds 200 ppm.

The average total content of rare earth elements ( $\Sigma\text{REE}$ ) in zoned pyroxenes is 5.44 ppm in cores and 4.61 ppm in rims (Table 1). The ratio of light to heavy rare earth elements (LREE/HREE) in pyroxene cores ranges from 13.98 to 36.06, with an average of 24.33, whereas in rims, it ranges from 9.72 to 52.17, with an average of 28.79. According to geochemical data, the total content of large-ion lithophile elements (LILEs)—specifically Rb, Ba, Cs, and Sr—is 19.35 ppm in cores and 18.02 ppm in rims, with concentrations decreasing in the order  $\text{Rb} > \text{Ba} > \text{Cs} > \text{Sr}$ . High-field-strength elements (HFSEs), especially Th and Ti, show a gradual increase in concentration from pyroxene cores ( $\sim 0.05$  ppm) to rims ( $\sim 0.07$  ppm) when normalized to primitive mantle values (Figure 6). LILEs have high ionic potential and are readily dissolved and transported in silicate melts under high-pressure and high-temperature conditions. In contrast, HFSEs exhibit low solubility in melt, leading to relative enrichment of LILEs over HFSEs. Furthermore, in the chondrite-normalized diagram (Figure 7), enrichment of LREEs over HREEs is evident, along with a positive Eu anomaly and a negative Ce anomaly. The Eu/Eu\* ratio is found to be similar in both cores ( $\sim 0.79$ ) and rims ( $\sim 0.81$ ), whereas the Ce/Ce\* ratio is higher in cores

(~4.63) and lower in rims (~3.28). Similarly, the Sr/Y ratio is high in cores (~175.79) and low in rims (~108.68) of the zoned pyroxenes. The cores of zoned pyroxene are rich in these elements (siderophile), indicating its precipitation from high-salinity fluids prior to phase separation of ore-forming fluids. This compositional variation suggests that the core regions crystallized under relatively higher-pressure conditions or during stages of limited plagioclase fractionation. The enrichment of Sr and Y in the pyroxene cores reflects their lithophile nature rather than siderophile behavior, indicating that these elements were incorporated into the pyroxene structure during magmatic differentiation. Consequently, the observed chemical zoning is more plausibly attributed to magmatic evolution processes rather than direct precipitation from high-salinity hydrothermal fluids. In contrast, high-field-strength elements (HFSEs) are generally insoluble in hydrothermal fluids; therefore, the relatively higher concentrations of HFSEs in cores compared to rims—including Th and Ti in pyroxene cores—are believed to result from the dissolution of HFSE-bearing minerals, such as zircon. Furthermore, the oscillatory zoning observed in pyroxene may record variations in the pathways and flux of fluids through endoskarn veins [14,28].

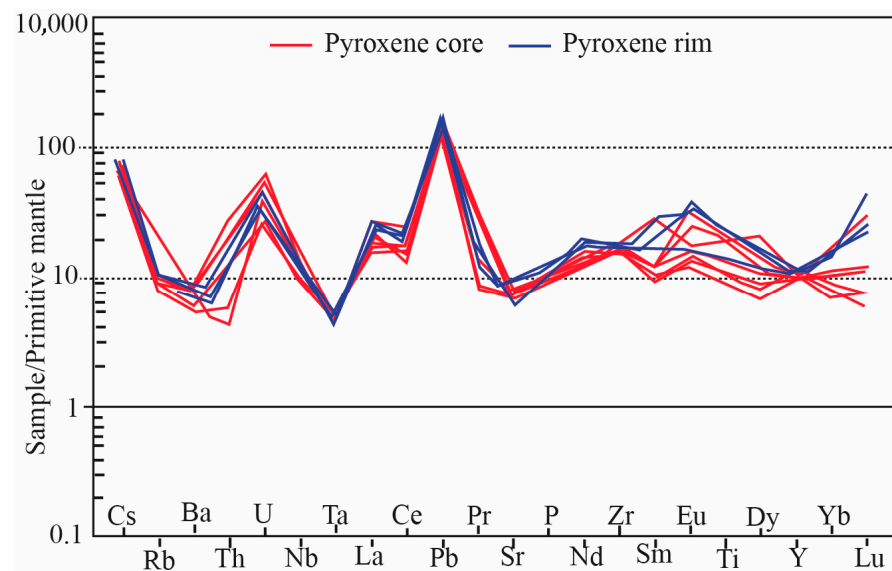


**Figure 6.** The normalized primitive REE diagram of zoned pyroxene [normalized values [39]].

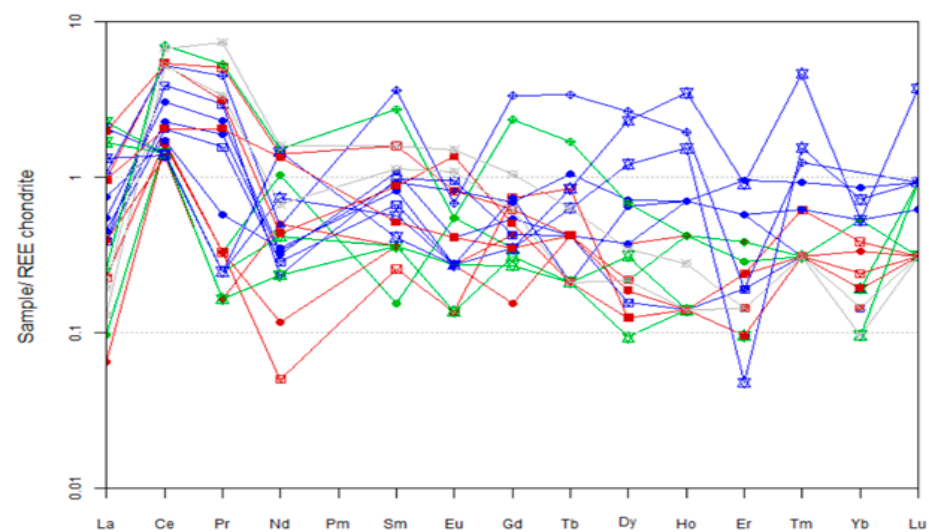


**Figure 7.** The normalized chondrite REE diagrams of zoned pyroxene [normalized values [39]].

#### 4. Discussion

The formation of skarn type mineralizations developed through magmatic–hydrothermal processes is largely controlled by oxidation state of magma, composition of exsolved “redox conditions”. Redox conditions, along with other factors, indicate that the composition and zoning of garnet and/or pyroxene can be dependent on local environment; however, thermal, compositional, and redox gradients established between causative intrusion and wall rocks play a particularly significant role in skarn formation. In skarn zones developed under influence of redox gradients, zoned minerals are inevitable [1]. Meinert [1] stated that pyroxene minerals in skarn-type deposits can be used to determine the deposit types and fluid characteristics. Therefore, even if all other parameters remain constant, pyroxene-dominated skarns are characteristic of reduced environments. The interaction of hydrothermal fluids, produced by a reduced wall rock and/or intrusion, suppresses garnet zoning while promoting development of pyroxene zoning [40]. Examination of thin sections from the studied skarn zone and zoned structure of pyroxene clearly indicates that hydrothermal fluids were characteristic of a reduced environment. Highly oxidized hydrothermal fluids derived from oxidized magma play a critical role in determining mineral assemblage and the metal carrying capacity of a system. One of the few studies that provides a detailed examination of the comprehensive fluid evolution process from the early to late stages of skarn formation is the investigation of the Baoshan deposit (South China) by Zheng et al. [26]. In their study, the researchers demonstrated that the fluid evolution during the development of the skarn mineralization system could be determined through the geochemical characteristics of pyroxene, garnet, and scheelite minerals, which are widespread in the skarn-forming stages. As noted in previous studies, diopside pyroxenes tend to crystallize under strongly oxidizing conditions [2,15,40,41], while the coexistence of magnetite and hematite commonly reflects such redox environments. In the skarn zone, association of magnetite with compositional features of pyroxene similarly indicate the presence of an oxidizing setting during mineralization. In thin sections of skarn zone, a high FeO content is observed, and it occurs together with magnetite in interstitial spaces between minerals. In this context, the mineralogical and geochemical data obtained provide a basis for interpreting processes controlling ore formation. Mineralization (Fe–Ti, Pb, Zn, and Cu) developed along the contacts between the Keban metamorphics and the Elazığ magmatic units. The zoning of diopside from the skarn zone, which is characterized by mineralization, consists of a homogeneous, Fe-poor core surrounded by Fe-rich and oscillatory-zoned rims. The composition and redox state of rocks in the study area—which includes graphitic schists as well as calcitic and minor dolomitic marbles (Figure 1)—represent unfavorable lithologies for skarn formation. This explains development of hedenbergite near the rim of zoned pyroxene. The formation of hedenbergite is partly influenced by the unfavorable redox conditions of the causative intrusion and unfavorable composition of wall rocks. A similar observation has been reported in the ilvaite-hedenbergite Fe deposits in Torre di Rio (Italy) [42]. In this study, we propose that the presence of strongly reducing conditions led Fe-rich hydrothermal fluid to transport predominantly  $\text{Fe}^{2+}$  complexes, which promoted the zoning of pyroxenes rather than garnet within the skarn assemblage.

The REE content of pyroxene provides information about surface adsorption, substitution mechanisms, growth rate, lattice energy, and fluid chemistry (composition, temperature, pH, and oxygen fugacity) [29]. Therefore, development of skarns, as well as origin and evolution of fluid, can be determined based on REE content of pyroxene or garnet [43]. The low content of large ion lithophile elements (LILE) is attributed to their larger ionic radii, while surface adsorption and crystal growth are controlled by kinetic mechanisms. The chemical composition of crystal is controlled by substitution and solid solution mechanisms. The zoning, which occurs during growth, reflects changes in major and trace elements.

Pyroxene zoning is significant in indicating development of hydrothermal fluids, diffusion processes between elements, and fluid chemistry in skarn deposits [44,45]. Mineral zoning typically develops through a two-stage growth process [33,46]. The first stage is controlled by diffusion-driven metasomatism occurring at low water/rock ratios and indicates mineral growth close to equilibrium. In contrast, the second stage is characterized by rapid mineral growth governed by metasomatism driven by advection during transport of magmatic fluids at high water/rock ratios. This process is facilitated by the fracturing of magmatic rock. Jamtveit [44] suggests that progressive compositional changes in growth zones may be caused by rapid transformation of hydrothermal fluid composition. The BSE image displays that the chemical change in the core to rim is sudden, not gentle, and therefore supports rapid crystallizing from hydrothermal solutions [44].

The concentrations of siderophile elements (Co and Fe) in hydrothermal fluids show a positive correlation with salinity. In our samples, the decreasing concentrations of siderophile elements (Fe) suggest that salinity of skarn-forming fluids decreased from the early to late stages, indicating a possible dilution or influx of less saline fluids during late stages of mineralization. The observed decrease in siderophile elements (e.g., Fe) from the core to rim, along with a progressive increase in Na content, suggests a temporal evolution of skarn-forming fluids from Fe-rich, high-temperature conditions toward more Na-enriched but Fe-depleted fluids in the late stage [46]. This trend may indicate fluid mixing, dilution, or a shift in fluid source—possibly from magmatic to more external, Na-bearing, lower-temperature fluids. The depletion of these elements in cores of endoskarn clinopyroxenes suggests that these minerals precipitated from hydrothermal fluids with relatively low salinity, prior to fluid phase separation [42,46]. High-field-strength elements (HFSEs) are generally insoluble in hydrothermal fluids. The relatively high concentrations of HFSEs in diopside cores can be explained by the presence of HFSE-bearing minerals such as zircon and monzonite in granitoids, and their dissolution leads to an increase in HFSEs in fluids [46].

The uranium content of the analyzed pyroxene is relatively low, which indicates that it did not crystallize in a reduced environment. The andradite–grossular composition of garnets in Elaziğ magmatic skarns suggests that the redox condition of the skarn-forming fluids was oxidized. This is because  $\text{Fe}^{2+}$ , which is preserved in reduced environments, is incorporated into the andradite structure. This is consistent with observed uranium (0.01–0.24 ppm) results. The uranium content in the pyroxene is related to the redox state of fluid [46]. Although the  $\text{Eu}^{3+}/\text{Eu}^{2+}$  ratio is used to determine the redox state of hydrothermal fluid, it can only be determined under conditions of temperatures exceeding  $>250^\circ\text{C}$ , low pressure, and low pH [47]. Bau [29] showed that under neutral pH conditions, low LREE, high HREE, and negative Eu anomalies occur. Under acidic pH conditions, high LREE, low HREE, and positive Eu anomalies are observed. A positive Eu anomaly is a significant indicator of high-temperature conditions [46,47]. Changes in  $\Sigma\text{REE}$  and high Ce and Nd content in hydrothermal fluid are directly proportional to changes in pH. As the water/rock (W/R) interaction increases,  $\Sigma\text{REE}$  also increases. The fact that zoned pyroxene cores have lower REE content compared to their rims indicates that the core of our pyroxene sample crystallized in a closed system, while the rims crystallized in an open system [48].

## 5. Conclusions

1. This study presents the first detailed documentation of oscillatory and growth zoning in pyroxenes from polymetallic skarn zones in the Elaziğ region, highlighting compositional variations from the core to the rim.
2. Skarns develop along contacts between dioritic and granitic plutonic rocks and carbonate rocks, forming two main zones: a narrow endoskarn and a more extensive ex-

oskarn. Endoskarns exhibit distinct mineralogical zoning, including pyroxene–garnet, pyroxene–scapolite, and epidote–garnet assemblages, whereas scapolite occurs in both endoskarn and exoskarn zones.

3. Pyroxenes are predominantly composed of diopside, with cores enriched in SiO<sub>2</sub> and MgO and rims enriched in FeO and CaO, reflecting magmatic differentiation and metasomatic processes. Minor serpentinized olivine within endoskarns is attributed to localized magnesium enrichment.
4. Cu–Fe skarns show low Mn/Fe ratios (<0.1) and low Zn content (~200 ppm), Fe skarns exhibit high Mn/Fe ratios (>0.2) and elevated Zn (>200 ppm), and W-bearing skarns display intermediate Mn/Fe (~0.15) and high Zn (>500 ppm). These correlations demonstrate that Mn/Fe ratios and Zn content in pyroxenes are effective indicators of skarn-forming environment.
5. Oscillatory and compositional zoning in pyroxenes provides key information on physicochemical conditions, fluid–rock interactions, and hydrothermal fluid evolution during skarn formation, offering a better understanding of magmatic and metasomatic processes controlling polymetallic skarn mineralization.
6. The low uranium content in pyroxenes (0.01–0.24 ppm) and andradite–grossular composition of garnets indicate that skarn-forming fluids were relatively oxidized. This is consistent with the incorporation of Fe<sup>2+</sup> into andradite and confirms that pyroxenes did not crystallize under reduced conditions.
7. Variations in ΣREE, Ce, Nd, and Eu anomalies reflect changes in fluid pH and temperature. The lower REE contents in pyroxene cores compared to rims suggest crystallization in a closed system for cores and an open system for rims, highlighting the influence of water/rock interaction on element mobility during skarn formation.

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