

Article

Sulfur and Carbon–Oxygen Isotopic Geochemistry and Fluid Inclusion Characteristics of the Yolindi Cu-Fe Skarn Mineralization, Biga Peninsula, NW Turkey: Implications for the Source and Evolution of Hydrothermal Fluids

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Abstract: The current study sought to investigate the physiochemical conditions and fluid evolution within the Yolindi Cu-Fe skarn mineralization located in the Biga Peninsula, NW Turkey. This was accomplished through a comprehensive investigation of geological and mineralogical data, along with isotopic analyses of sulfur ($\delta^{34}\text{S}$), carbon ($\delta^{13}\text{C}$), and oxygen ($\delta^{18}\text{O}$) of sulfide and calcite minerals, respectively, as well as fluid inclusion data pertaining to various minerals (e.g., andradite, quartz, and calcite). The Yolindi area features a complex geological framework, including the Paleozoic Kalabak Group (which includes the Torasan, Yolindi, and Sazak formations) and the Triassic Karakaya Complex. These formations were subsequently intruded via Early Miocene Şaroluk granitoids and Hallaçlar volcanics. Skarn formation is zoned into endoskarn and exoskarn types (being categorized into proximal, intermediate, and distal zones), with distinct mineral assemblages indicating concentric and contact metamorphic alteration patterns around the western part of Şaroluk granitoid intrusion in contact with the Torasan formation. The ore mineralogy and paragenesis suggest three distinct stages of evolution: an initial phase of prograde metasomatism characterized by the formation of magnetite and pyrite alongside anhydrous calc-silicate minerals; a subsequent phase of retrograde alteration marked by the formation of epidote, actinolite, and scapolite, accompanied by the occurrence of chalcopyrite and specular hematite; and finally, a post-metasomatic stage involving oxidation processes that led to the development of secondary mineral assemblages containing cerussite, covellite, and malachite. Sulfur isotopes ($\delta^{34}\text{S}$) of sulfides from endoskarn (from +0.27 to +0.57‰ VCDT) to intermediate exoskarn (from −9.44 to −5.46‰ VCDT) zones indicate a diverse sulfur source, including magmatic, sedimentary, and possibly organic matter. $\delta^{34}\text{S}$ values in hydrothermal fluids suggest a magmatic–hydrothermal origin, with endoskarn and proximal zone fluids showing a slight negative signature and intermediate zone fluids indicating a strong influence from organic-rich or metamorphic sulfur reservoirs. Carbon and oxygen isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of calcite revealed a progression from marine carbonate signatures in marble samples (from +1.89 to +2.23‰ VPDB ; from +21.61 to +21.73‰ VSMOW) to depleted values in prograde (from −6.0 to +0.09‰ VPDB ; from +6.22 to +18.14‰ VSMOW) and retrograde skarns (from −3.8 to −2.25‰ VPDB ; from +0.94 to +3.62‰ VSMOW), reflecting interactions with high-temperature magmatic fluids and meteoric water mixing. The fluid inclusions in prograde minerals generated under the conditions of fluid boiling exhibited high temperatures, reaching up to 412 °C, and salinities up to 26 wt.% NaCl equivalent. Conversely, the fluid inclusions in retrograde minerals, which were generated due to fluid mixing, exhibited lower temperatures (with an average of 318 °C) and salinities with an average of 4.9 wt.% NaCl equivalent. This indicated that the cooler and more diluted fluids mix with meteoric waters and interact with organic materials in the host rocks. This suggests a multifaceted origin involving various sources and processes. Therefore, this study concluded that the skarn mineralization in the Yolindi area resulted from complex interactions between magmatic, metamorphic, and meteoric



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fluids, reflecting a dynamic ore-forming environment with implications for the regional metallogeny of Cu-Fe skarn deposits.

Keywords: mineralogy; skarn evolution and zonation; sulfur isotopes ($\delta^{34}\text{S}$); carbon isotopes ($\delta^{13}\text{C}$); oxygen isotopes ($\delta^{18}\text{O}$); fluid inclusions; Yolindi Cu-Fe Skarn; Biga Peninsula; NW Turkey

1. Introduction

Skarn deposits are a noteworthy category of mineral resources that result from the complex geological interaction of magmatic, hydrothermal, and metasomatic processes [1]. The Biga Peninsula in northwestern Turkey is particularly rich in such deposits, with Fe skarns and Cu skarns being prominent [2–5]. Fe skarns are often associated with the regional Oligocene to Lower Miocene granitoids and often occur with porphyry copper or epithermal gold deposits [3,6–9]. These skarns have a high iron content and may also display copper enrichment, especially in areas where magnetite undergoes alteration to hematite. In addition, Cu skarns have often been identified by the presence of garnet–pyroxene and wollastonite–garnet skarns in the endoskarn zones and wollastonite–garnet skarns in the exoskarn zones [3]. The formation of these deposits has been closely associated with intrusions, such as granodiorite, monzodiorite, and quartz diorite, that interact with their surrounding sedimentary and volcanosedimentary rocks [3]. The observed variation in mineral composition, which ranges from endoskarns within the intrusive bodies to exoskarns in the surrounding country rocks, is a direct consequence of the differences in fluid composition, pressure, and temperature that occurred during their formation [1,3,10].

The Yolindi area is situated in the northeastern part of the Biga Peninsula, which is located in the western sector of the Sakarya Zone in northwest Turkey (Figure 1). The tectonic activity of the Biga Peninsula is mainly influenced by the movement taking place along the North Anatolian Fault Zone [11]. This fault zone splits into two main branches, known as the northern and southern branches, which are situated in the eastern region of Marmara. The main tectono-stratigraphic formations in the area of the Biga Peninsula consist of the Denizgoren ophiolite and the Çetmi ophiolitic mélangé, located in the southwestern and northern parts of the Biga Peninsula, respectively [2,12]. During the Mesozoic period, the peninsula saw significant tectonic activities, such as sedimentation, the emplacement of ophiolites, and the formation of volcanic island arcs. The process of sedimentation played a crucial role in shaping the geological features of the region throughout the Triassic period [12]. It included the accumulation of carbonate rocks, namely limestones and dolomites, in shallow marine environments. During the transition from the Mesozoic era to the Jurassic and Cretaceous periods, there was a spreading of ophiolite complexes, flysch, and mélangé deposits due to tectonic activity. In addition to the metamorphic basement rocks, the Biga Peninsula encompasses a comprehensive geological history of magmatic and volcanic activity that extends from the pre-Cenozoic to the Cenozoic periods [12]. The emplacement of granitic intrusions and volcanic rocks occurred in the Biga Peninsula during the Late Paleozoic period as a result of the closing of the Paleo-Tethys Ocean and the evolution of the supercontinent Pangea [13]. The volcanic rocks, together with their associated mineral deposits, provide crucial insights into the tectonic and magmatic processes that occurred in the area throughout the Late Paleozoic period. In the Cenozoic era, there were several intrusions that occurred from the Eocene to the Oligo-Miocene periods. These intrusions include Dikmen, Evciler, Eybek, Kestanbol, Kuşçayır, Şaroluk, and Yenice [7,8,14–19]. They were mostly found in the middle and southern areas of the peninsula. Meanwhile, the Ayvacık volcanic rocks, Ezine basalt, and Taştepe basalt represent the Cenozoic volcanic rocks. These rocks exhibit calc-alkaline to alkaline affinities, suggesting a varied history of magmatic activity [15,20,21]. The Cenozoic plutons and volcanic successions of the Biga Peninsula have both geological and economic importance.

They are responsible for the bulk of the metallic mineral resources and industrial materials that have contributed to this region's economy [2,22].

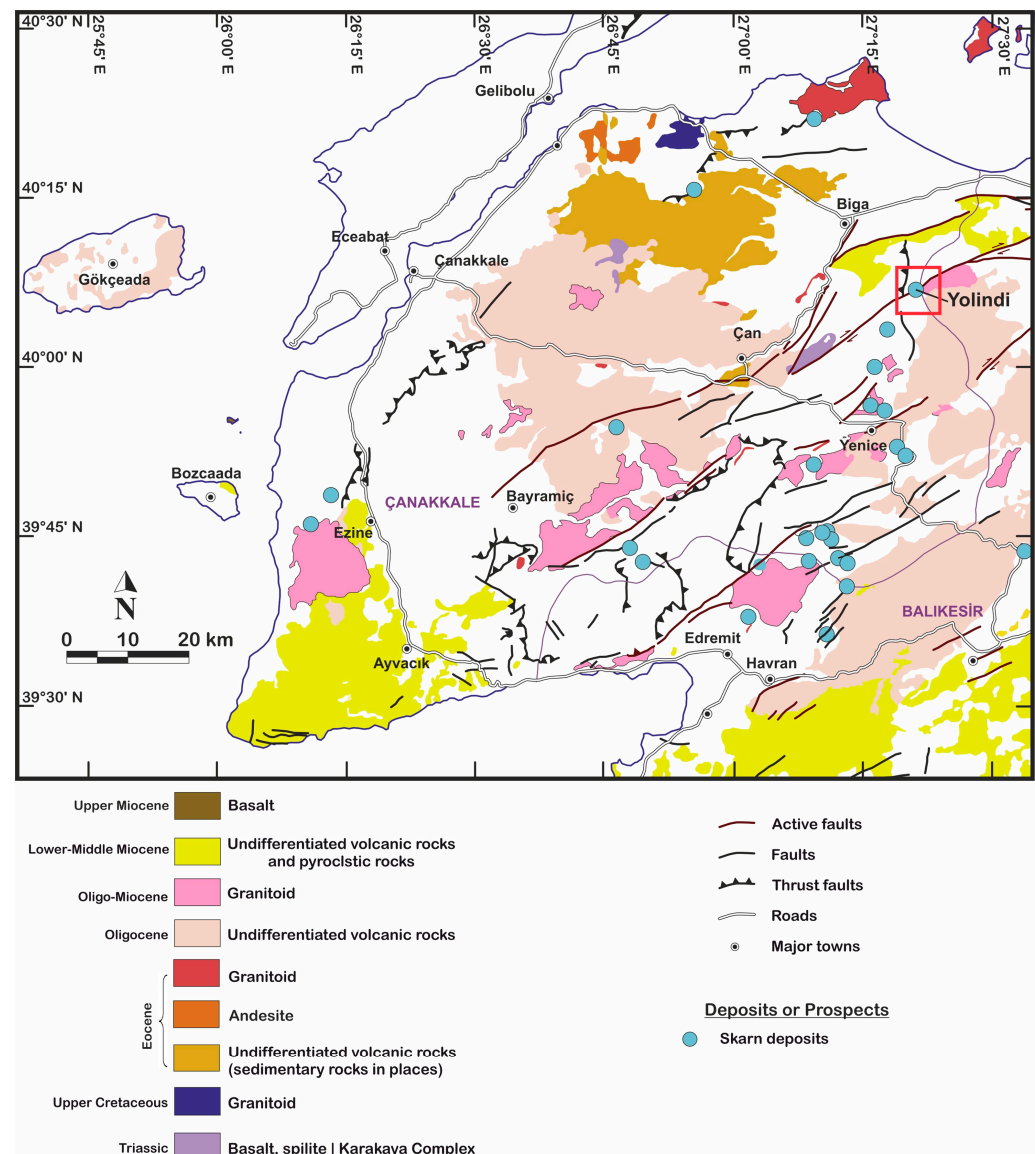


Figure 1. The spatial distribution of skarn deposits on the Biga Peninsula, located in northwestern Turkey, modified according to Yigit [2], Kuşçu [3], and Kaya et al. [4]. The red box refers to Figure 2.

This study utilized a multidisciplinary method, integrating microthermometry of fluid inclusions and several isotopic data types, to investigate the physiochemical conditions and fluid evolution within the Yolindi Cu-Fe skarn mineralization. In sulfide minerals, sulfur isotopes ($\delta^{34}\text{S}$) can be used to identify sulfur sources, whereas carbon ($\delta^{13}\text{C}$) and oxygen isotopes ($\delta^{18}\text{O}$) in calcite minerals provide information regarding the composition and temperature of fluid–rock interactions. Moreover, the fluid inclusions within various minerals formed at distinct phases of skarn mineralization provide a direct record of the physical and chemical conditions, allowing to figure out how pressure, temperature, and compositional evolution have changed throughout the skarn formation.

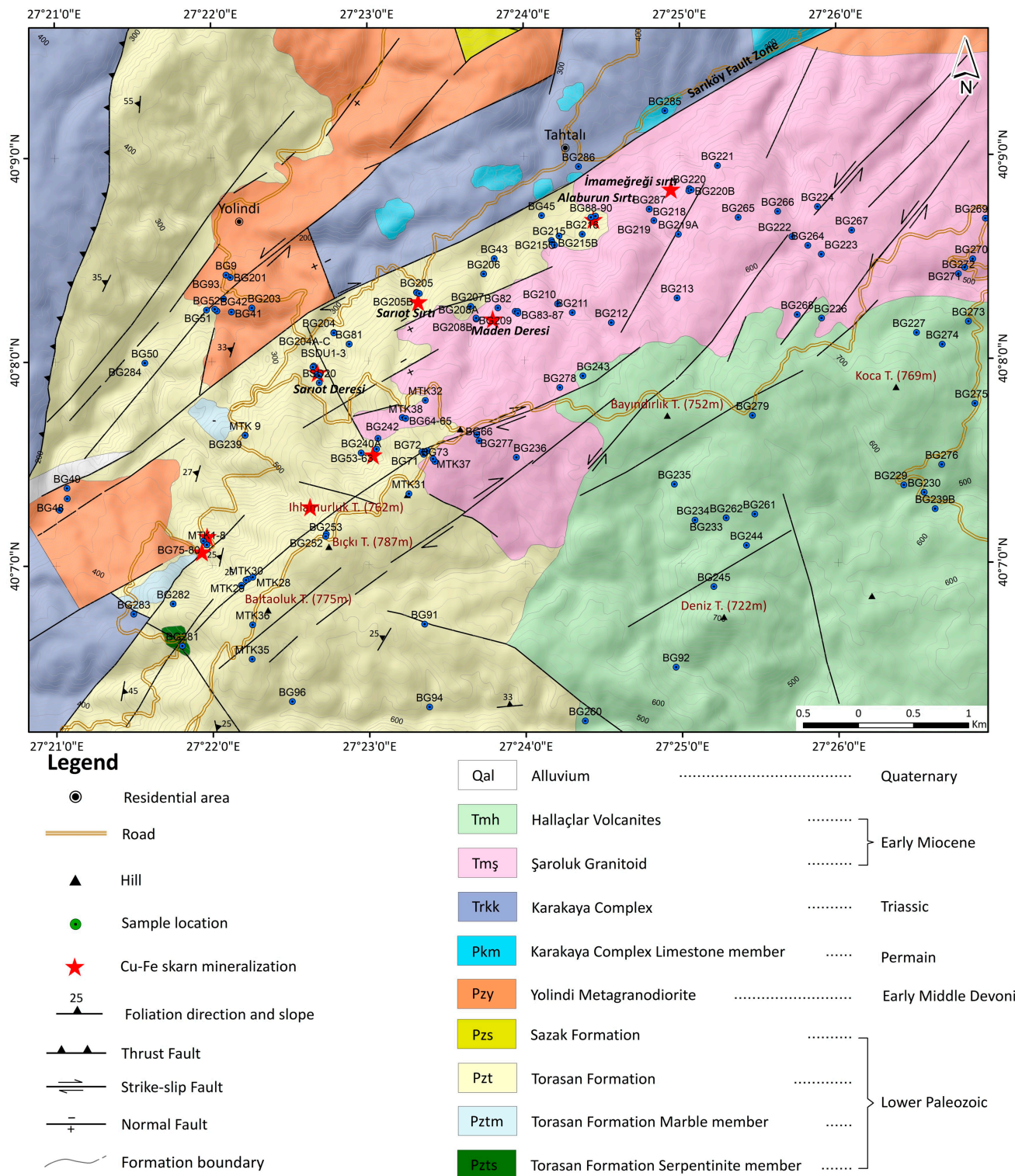


Figure 2. Geologic map of the Yolindi area (modified according to Duru et al. [23], Aysal [24], Aysal et al. [25], and Kaya et al. [4]).

2. Geology of the Yolindi Area

The Yolindi area is located NE of the Biga Peninsula in Çanakkale province, NW Turkey (Figure 1). It comprises the Paleozoic Kalabak Group and Triassic Karakaya Complex, which were subsequently intruded by the Early Miocene Şaroluk granitoids and Hallaçlar volcanics (Figure 2).

The Kalabak Group forms the basement of the Sakarya Zone, which is a distinct tectonic unit that includes the Torasan formation at the base and the Sazak formation at the top, later intruded by Yolindidi metagranodiorite (Figure 2). The Lower Paleozoic Torasan formation (Pzt) is located in the western study area, in close proximity to Yolindi village, Bıçkı, and Baltaoluk hill (Figure 2). Phyllites, muscovite, biotite, talc, tremolite, and chlorite schists, along with their associated tuffs, constitute the majority of this formation, along with actinolite hornfels, metasandstone, and metasiltstone. Phyllites contain serpentinized peridotites (Pzts) (Figure 3a) and marble members (Pztm) as their blocks and lenses, respectively. Phyllites have a distinct foliation consisting of muscovite, biotite, and quartz, together with opaque minerals (Figure 3b). Actinolite hornfels are composed of actinolite, quartz, clinozoisite, clinopyroxene, and opaque minerals (Figure 3c). The composition of serpentinite lenses primarily consists of antigorite, chlorite, and clinopyroxene, along with a small amount of opaque minerals (Figure 3d). Marble and recrystallized limestone are characterized by a fine-grained texture and are primarily composed of calcite (Figure 3e). The Yolindi metagranitoids (Pzy) have been determined to be of early Middle Devonian ages using U-Pb zircon SHRIMP and LA-ICP-MS dating techniques, as reported by Aysal et al. [25]. The study area in Yolindi village has prominent outcrops to the north (Figures 2 and 3f). These rocks include biotite gneiss and metagranodiorite. Biotite gneiss consists of biotite, quartz, sericitized plagioclase, and opaque minerals (Figure 3g). Metagranodiorite is composed of plagioclase that has undergone sericitization, together with quartz, biotite, and opaque minerals (Figure 3h). The Triassic Karakaya Complex (Trkk) is located in the middle and western parts of the study area, close to the villages of Inova and Tahtali (Figure 2). It is made up of marble, metasandstone, phyllite, metavolcanics, and serpentinites [4].

The Şaroluk granitoid (TmŞ) is a 20 km² elliptical pluton that is oriented in an east–west direction (Figure 2). The U-Pb zircon dating conducted by Aslan et al. [26] revealed that the Şaroluk pluton originated from magmatic activity during the Early Miocene period, between 22.18 ± 0.40 and 21.51 ± 0.37 Ma. Aysal [27] reported an accurate date of 23.97 ± 0.53 Ma for the same event. A hornfels zone evolved in the Torasan formation along the western boundary of the Şaroluk intrusion (Figure 3i). The Şaroluk pluton mostly consists of quartz monzonite, with some granodiorite. Quartz monzonite consists of biotite, tremolite, actinolite, K-feldspar, quartz, and biotite with tremolite (Figure 3j). Granodiorite is composed of plagioclase (50%–70%), quartz (20%–30%), microperthite (5%–15%), hornblende, biotite, small quantities of pyroxene, and opaque minerals (Figure 3k).

The Hallaçlar formation (Tmh) is found in the southwest of the study area, around Beyoluk village, Bayındırlık Hill, Koca Hill, and Deniz Hill (Figure 2). It was dated at 23.6 Ma by Krushensky [28], 26.5 ± 1.1 Ma by Dönmez et al. [29], and 22.6 ± 0.8 Ma by Karacik et al. [30], indicating volcanic activity from the Late Oligocene period to the Early Miocene period. Rhyodacite, felsic tuffs, tuffaceous siltstone, and pyroclastics are included. Porphyritic andesite mainly comprises hornblende, biotite, and plagioclase phenocrysts embedded in fine-grained microcrystalline groundmass of plagioclase laths, quartz, and opaque minerals (Figure 3l).

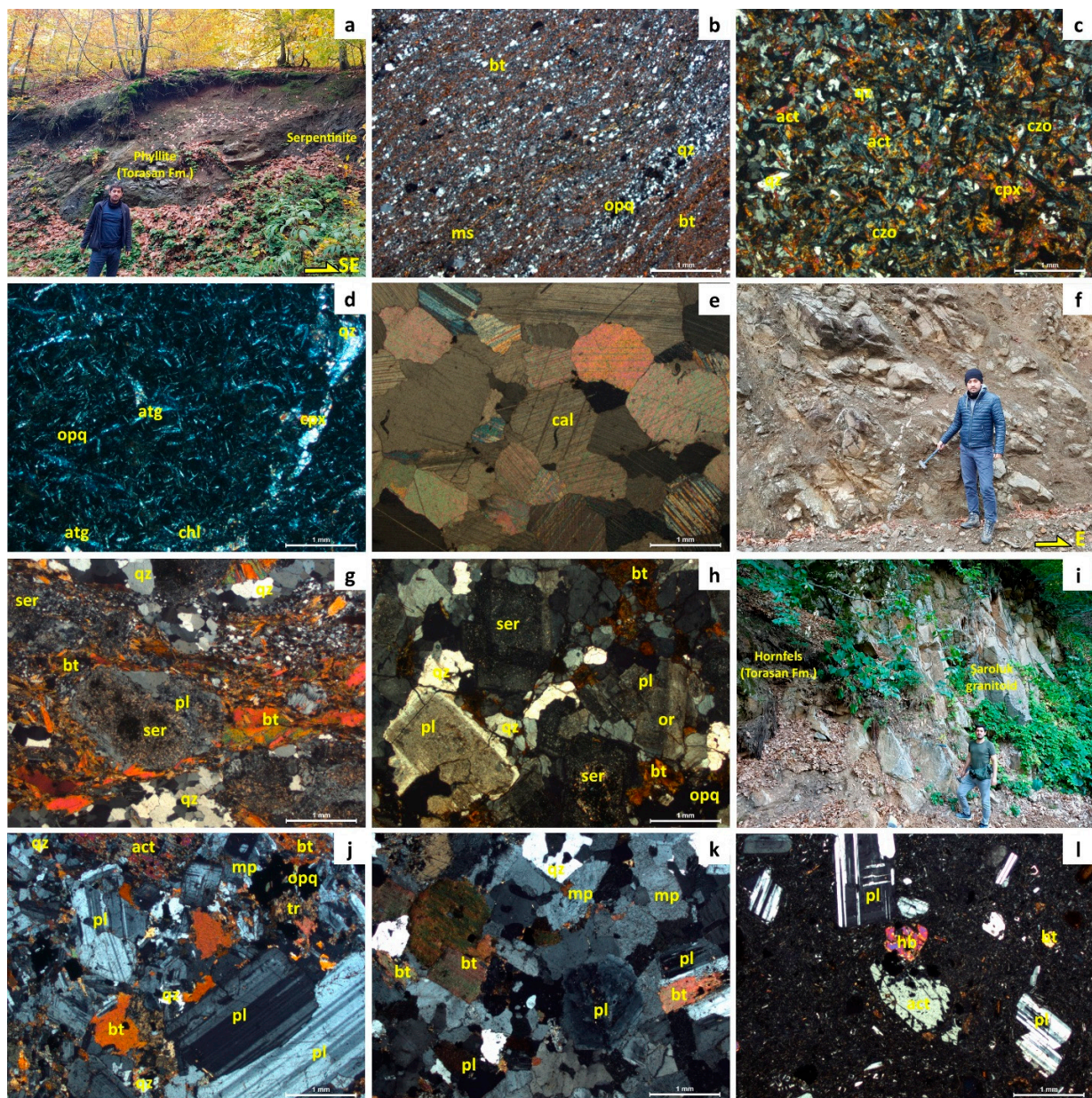


Figure 3. (a) Serpentinized peridotites within the Torasan formation. (b) Phyllite exhibits well-developed muscovite, biotite, and quartz foliation with opaque minerals. (c) Actinolite and quartz in actinolite hornfels with clinozoisite, clinopyroxene, and opaque minerals. (d) Serpentinites are made up of antigorite, chlorite, clinopyroxene remnants, and other less frequent opaque minerals. (e) The major component of marble is calcite. (f) General view of the Yolindi metagranitoids. (g) Biotite gneiss contains biotite in addition to quartz, sericitized plagioclase, and other opaque minerals. (h) Sericitized plagioclase, quartz, biotite, and opaque minerals are found in metagranodiorite. (i) At the border of the Şaroluk granitoids, a hornfels zone formed inside the Torasan formation. (j) The majority of quartz monzonite is composed of plagioclase, K-feldspar, quartz, biotite, actinolite, and tremolite. (k) Granodiorite contains plagioclase, quartz, and microperthite, as well as hornblende, biotite, and other opaque minerals. (l) Porphyritic andesite with hornblende, actinolite, biotite, and plagioclase phenocrysts embedded in fine-grain microcrystalline plagioclase laths, biotite, hornblende, quartz, and opaque minerals. Abbreviations: actinolite (act), antigorite (atg), biotite (bt), calcite (cal), chlorite (chl), clinopyroxene (cpx), clinozoisite (czo), hornblende (hb), microperthite (mp), muscovite (ms), orthoclase (or), opaque mineral (opq), plagioclase (pl), quartz (qz), and sericite (ser).

3. Deposit Geology of the Yolindi Cu-Fe Skarn Mineralization

The Yolindi Cu-Fe ($\pm$ Zn $\pm$ Pb) skarn mineralization exhibits zonal alteration patterns that can occur either in a concentric manner or perpendicular to the contact between the Şaroluk granitoid intrusion and the Torasan formation, as well as carbonate-rich rock or limestone. The zones are categorized as endoskarns and exoskarns, which can be further subdivided into three zones based on their distance from the intrusive body: proximal, intermediate, and distal zones (Figure 4). These zones exhibit distinct mineral assemblages (Figure 4).

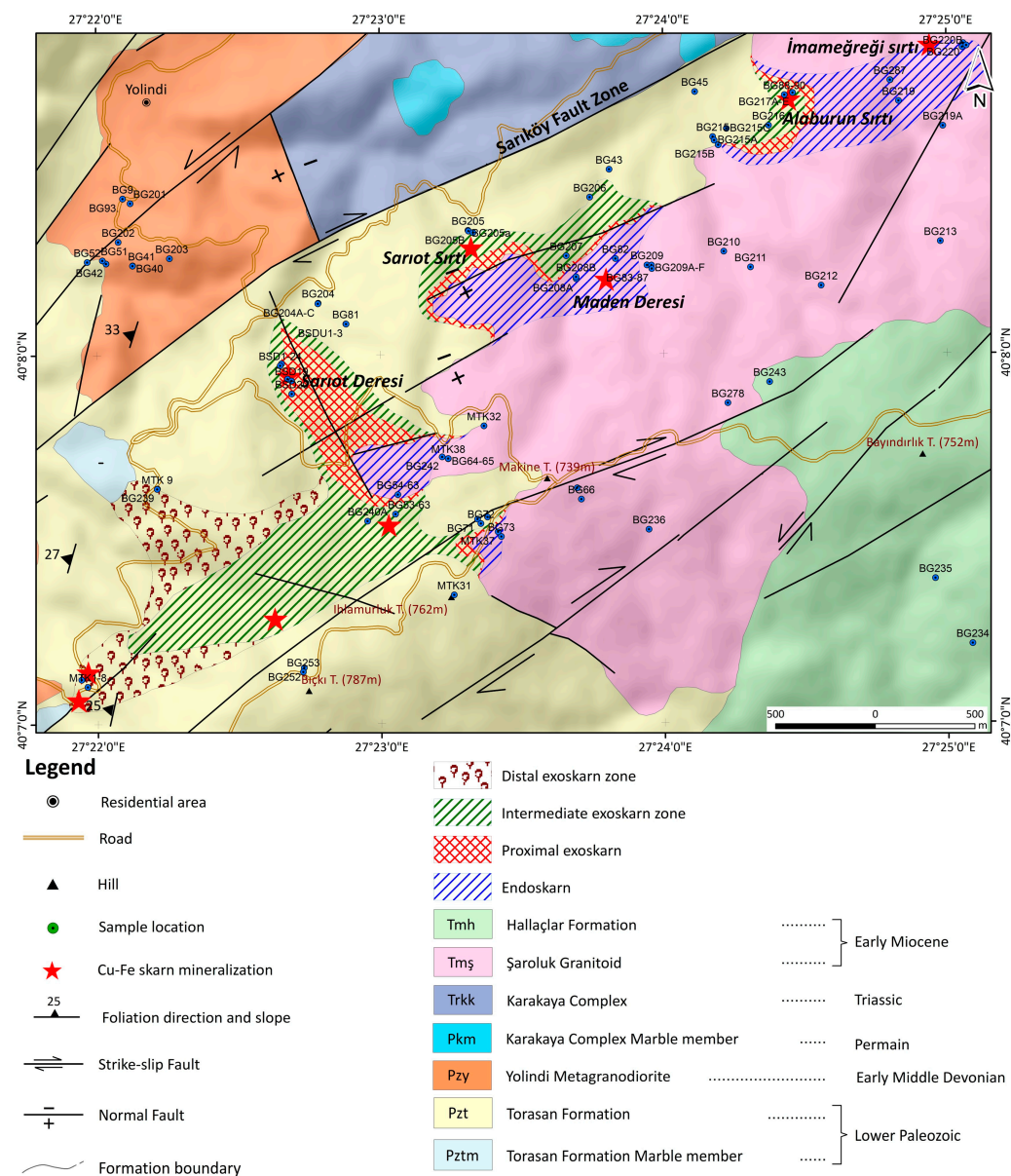


Figure 4. The zonation map of the Yolindi Cu-Fe Skarn mineralization illustrates several skarn zones, including the endoskarn and the proximal, intermediate, and distal exoskarn zones [4].

The Şaroluk quartz monzonite has undergone bleaching along the boundaries between the Torasan formation and the Şaroluk intrusion. This is evident in the field through the presence of the endoskarn zone (Figures 4 and 5a). The formation of endoskarn occurs within the Şaroluk intrusive body itself, usually in its outer parts. It has been specifically noticed near the Maden Deresi and İmameğreği Sirtı areas (Figure 4). On a mesoscopic scale, the occurrences of skarnized granitoids (which include andradite) can refer to the garnet

formation, followed by epidote and sericite, during metasomatism. In the Maden Deresi area, there was a transition from granodiorite containing magnetite that has undergone a few alterations to endoskarn containing magnetite, with the degree of alterations rising towards the contact region (Figure 5a). The magnetite-bearing granodiorites comprise quartz, plagioclase, microperthite, biotite, hornblende, pyroxene, and sphene, along with magnetite (Figure 5b). The magnetite-bearing endoskarn is characterized by the presence of andradite and epidote minerals, together with magnetite and goethite (Figure 5c). The İmameğreği Sirtı area is recognized by the presence of magnetite- and pyrite-bearing granodiorite with quartz, plagioclase, microperthite, biotite, diopside, actinolite, and sphene, along with magnetite, pyrite, and hematite (Figure 5d).

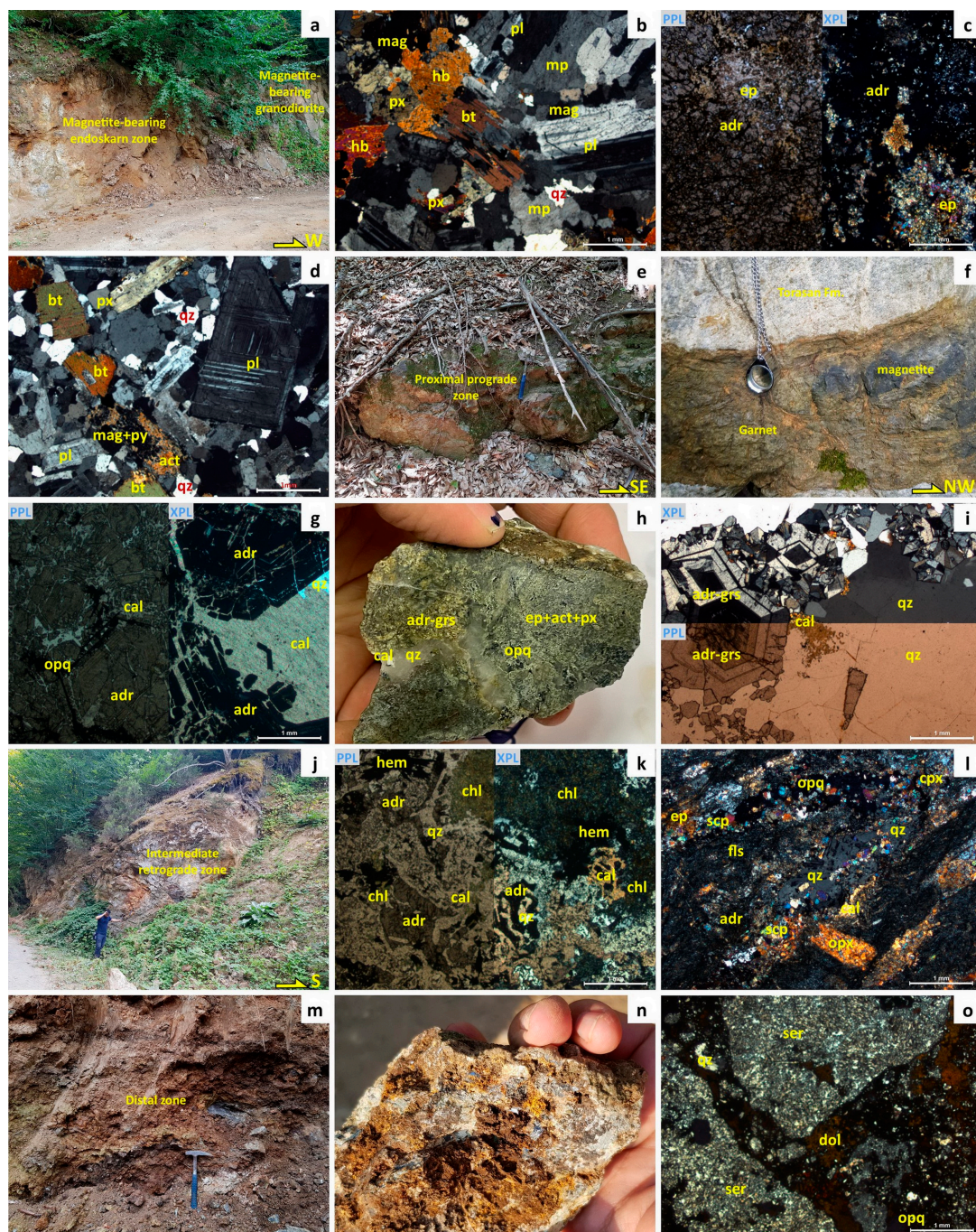


Figure 5. (a) General characteristics of the endoskarn zone within the Şaroluk intrusion in Maden Deresi. (b) Magnetite-bearing granodiorites. (c) Magnetite-bearing endoskarns with andradite and

epidote. (d) Magnetite- and pyrite-bearing granodiorite containing quartz, plagioclase, microperthite, biotite, and actinolite as opaques, as well as magnetite and pyrite. (e,f) Garnet- and magnetite-bearing prograde proximal zones within the Torasan formation. (g) In the proximal zone, andradite, calcite, and quartz occur. (h) The retrograde proximal zone's greenish tint, which has been cut with a quartz carbonate vein. (i) In the retrograde proximal zone, andradite–grossular intergrowth, calcite, and quartz occur. (j) Green and brown color alteration of the intermediate exoskarn zone. (k,l) In the intermediate exoskarn zone, garnet (andradite–grossular), pyroxenes, scapolite, and calcite coexist with opaque minerals. (m–o) Sericite and carbonate alteration of the distal exoskarn zone. Abbreviations: actinolite (act), andradite (adr), biotite (bt), calcite (cal), chlorite (chl), clinopyroxene (cpx), dolomite (dol), epidote (ep), feldspar (fls), grossular (grs), hematite (hem), hornblende (hb), magnetite (mag), microperthite (mp), orthopyroxene (opx), plagioclase (pl), pyroxene (px), pyrite (py), quartz (qz), scapolite (scp), and sericite (ser).

The exoskarns located around the Şaroluk granitoid body in the Torasan formation usually have magnetite, pyrite, epidote, scapolite, garnet, pyroxene, chalcopyrite, bornite, hematite, and sometimes sphalerite and galena. Meinert [31] classified these zonal patterns into three subzones: proximal, intermediate, and distant zones.

The earliest phase of the skarn system is the proximal prograde exoskarn zone, characterized by a high concentration of garnet and magnetite in the Sariat Deresi area (Figure 4). It has been distinguished by zones of dark garnet (zoned andradite) and magnetite zones with subordinate hematite (martitization) throughout the hornfels rocks of the Torasan formation (Figure 5e–g). The proximal retrograde exoskarn zone located in the northwest of the Sariat Deresi area is distinguished by its greenish color and having retrograde minerals like epidote and actinolite, along with clinopyroxene relics and andradite–grossular intergrowth that are intersected by quartz–carbonate veins (Figure 5h,i).

The intermediate exoskarn zone underwent development in the Sariat Sirtı, İhlamluk Tepe, and Alaburun Sirtı areas within the Torasan formation (Figure 5j). This area is rich in garnet, pyroxene, calcite, and scapolite. This zone exhibits distinct characteristics that indicate a gradual transition from the hot, magma-influenced area located closer to the source to the cooler, more distant area with retrograde processes. Minerals such as epidote, scapolite, and chlorite are frequently formed (Figure 5k,l), suggesting a shift from high-temperature minerals to lower-temperature and retrograde minerals, which is caused by changes in temperature and fluid composition during the evolution of skarn, including chalcopyrite, pyrite, and specular hematite.

In addition, the distal exoskarn zone is located farthest from the Şaroluk granitoid pluton inside the Torasan formation in the Bıçkı Tepe area (Figure 4). It encompasses distinct mineral compositions, including epidote, chlorite, calcite, dolomite, and sericite (Figure 5m–o), along with galena, sphalerite, and a lesser amount of chalcopyrite with cerussite, covellite, and malachite.

4. Sampling and Analytical Methods

A comprehensive fieldwork project was conducted in the Yolindi area to gain a thorough comprehension of the geological setting. In order to ensure that the samples were representative, they were systematically collected from both the main host rocks and the altered rocks that exhibited mineralization. A total of 121 thin sections and 88 polished sections were meticulously prepared. These sections underwent a petrographic examination using a polarizing microscope to ascertain the mineralogical and textural relationships within the rocks.

Thirty-four mineralized samples were carefully selected from various skarn zones with the specific aim of evaluating sulfur isotope data on sulfide minerals. A total of six pyrite samples were obtained from the endoskarn zone, consisting of three pyrite and three chalcopyrite samples from the prograde proximal exoskarn zone, ten pyrite and three chalcopyrite samples from the retrograde proximal exoskarn zone, and seven pyrite and two chalcopyrite specimens from the intermediate exoskarn zone. The initial preparation

of these selected samples comprised the procedure of grinding and sieving to obtain a consistent mesh size of 2 mm, ensuring uniformity in the granularity of these samples. Individual mineral grains were carefully handpicked under a binocular microscope to guarantee the purity of the sample set for isotopic analysis. The total sulfur content and sulfur isotopic composition ($\delta^{34}\text{S}/\delta^{32}\text{S}$ ratios) of the samples were determined using elemental analysis coupled with isotope ratio mass spectrometry (EA/IRMS) at the Iso-Analytical Laboratory in Sandbach, UK. The isotope data were expressed as $\delta^{34}\text{S}$ values that were standardized to the Vienna Cañon Diablo Troilite (VCDT) standard. The addition of vanadium pentoxide (V_2O_5) to the samples was performed in order to enhance the combustion characteristics. The International Atomic Energy Agency (IAEA) distributes NBS-127, IAEA-S-1, and IAEA-SO-5 as inter-laboratory comparison standards, which have globally recognized $\delta^{34}\text{S}$ values. For cross-validation, the NBS-127, IAEA-S-1, and IAEA-SO-5 were used to accomplish analytical calibration. The measurement precision of the $\delta^{34}\text{S}$ results was verified to be within $\pm 0.3\%$ for all standards, with six duplicates each, thereby confirming correctness.

Isotopic compositions of carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) in calcite minerals were determined from a diverse suite of samples, including marble ($n = 5$), retrograde skarn ($n = 9$), and prograde skarn ($n = 11$). Each carbonate sample, precisely weighed between 0.2 and 0.6 mg using a sensitive balance, underwent a reaction with approximately 0.1 mL of 99% orthophosphoric acid (MERCK) at a constant temperature of 25 °C on an autosampler table. The resultant CO_2 gas, after being liberated from the carbonate samples, was processed using the gas bench continuous flow isotope ratio mass spectrometry technique. The isotopic ratios were analyzed utilizing a Thermo Finnigan Deltaplus XP isotope ratio mass spectrometer (IRMS) (Thermo Fisher Scientific, Waltham, MA, USA), with the isotopic ion ratios converted into raw isotope data using ISODAT 2.0 software. The international standard NBS19 Limestone (NIST), with known $\delta^{13}\text{C}$ of 1.95‰ and $\delta^{18}\text{O}$ of -2.20% , served as the primary reference for calibrating the crude isotope measurements to true values, anchored to the VPDB (Vienna Pee Dee Belemnite) standard. Measurements were conducted with a precision of $\pm 0.2\%$ for both isotopes, reflecting high reproducibility and accuracy. These analyses were carried out at the METU Central Laboratory within the Stable Isotope Ratio Mass Spectroscopy Laboratory (DIL), ensuring robustness in the methodological approach and data integrity.

The fluid inclusion investigations were conducted in the Istanbul Technical University (ITU) fluid inclusions laboratory on 80- μm -thick, double-polished, thin sections of andradite, grossular, quartz, and calcite minerals. The measurements were acquired using a Linkam THMG-600 stage, which had the ability to both heat and freeze and was mounted on a Leica DM2500P optical microscope (Leica, Wetzlar, Germany). The microscope was outfitted with a video camera and a display. The temperature range for the measurements was from +600 to -200 °C. The calibration of this step was conducted with potassium dichromate, pure H_2O , CO_2 , and H_2O –NaCl standards. The microthermometric measurements for heating and freezing were performed with an accuracy of 0.4 °C for the freezing stage and 5.0 °C for the heating stage, using the standard approaches outlined by Roedder [32] and Shepherd et al. [33]. This study evaluated and recorded the homogenization temperature (T_h), eutectic temperature (T_e), and final melting temperature of ice ($T_{\text{m-ice}}$).

5. Results

5.1. Ore Mineralogy and Paragenesis

The ore mineralogy includes magnetite, pyrite, chalcopyrite, and specular hematite, with a subordinate amount of galena, sphalerite, cerussite, malachite, and goethite (Figure 6). Magnetite mostly occurred within the endoskarn in the magnetite-bearing granodiorite (Figure 6a) and magnetite-bearing endoskarn (Figure 6b), as well as throughout the proximal prograde exoskarn zone (Figure 6c), in association with pyrite, andradite, and augite minerals. It is distinguished by brownish crystals, which vary in shape from subhedral to anhedral and may reach diameters of up to 2 mm. Occasionally, it undergoes martitization,

a process in which magnetite is substituted with hematite as a result of oxidation (Figure 6c). In the study area, chalcopyrite was the predominant copper–iron sulfide mineral. It occurs in the proximal retrograde exoskarn zone in the northwest of Sariot Deresi, as well as in the intermediate zone. Subhedral crystals of a yellowish color are formed together with pyrite, hematite, and sphalerite (Figure 6d–f). Pyrite is made up of subhedral to euhedral light-yellow crystals that are 10 to 200 microns across in length. It frequently forms with magnetite in the endoskarn (Figure 6b), as well as in the proximal and intermediate exoskarn zones associated with chalcopyrite, hematite, and bornite (Figure 6d,e,g). Specular hematite is a kind of hematite that can be identified via its clusters of shiny, metallic, flat flakes or tabular crystals (Figure 6h). It is formed within the intermediate zone of the exoskarn, associated with chalcopyrite and pyrite (Figure 6e,f). Galena is distinguished by the occurrence of sizable, separate subhedral light gray crystals in the distal zone, which is encountered with sphalerite and undergoes an alteration to form cerussite (Figure 6j,k). In addition, the distal zone undergoes the alterations of galena, sphalerite, and chalcopyrite, leading to the formation of cerussite, covellite, and malachite, respectively (Figure 6j–l).

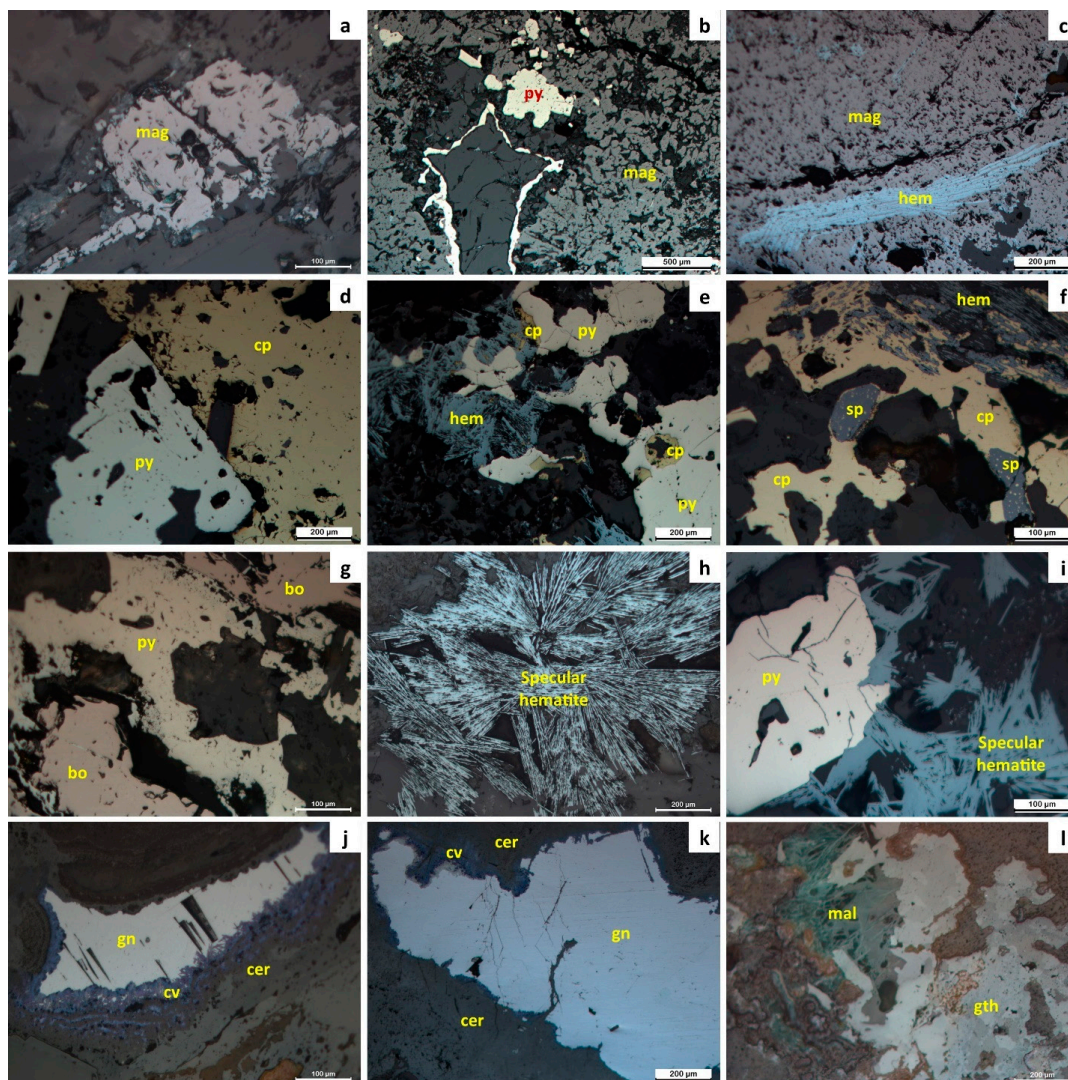


Figure 6. (a) Magnetite occurred within the granodiorite in Maden Deresi. (b) Magnetite and pyrite in magnetite-containing endoskarn. (c) Magnetite’s martitization to hematite in the proximal exoskarn zone. (d) Chalcopyrite and pyrite in the proximal retrograde zone. (e) In the retrograde proximal

zone, there is chalcopyrite, pyrite, and specular hematite. (f) Chalcopyrite occurs, along with sphalerite and specular hematite. (g) Pyrite with bornite in the proximal retrograde zone. (h) Clusters of specular hematite flakes that are shiny, metallic, and flat. (i) Specular hematite is seen in association with pyrite. (j,k) Cerussite and covellite are the alteration products of galena in the distal zone. (l) Malachite and goethite are the alteration products of chalcopyrite and pyrite, respectively, in the distal zone. Abbreviations: bornite (bo), cerussite (cer), chalcopyrite (cp), covellite (cv), galena (gn), goethite (gth), hematite (hem), magnetite (mag), malachite (mal), pyrite (py), and sphalerite (sp).

Paragenesis studies on the Yolindi Cu-Fe skarn mineralization process revealed that there were three distinct mineralization stages that were identified based on the contact relationships between the metamorphic, alteration, and ore minerals, as shown in Figure 7. The prograde stage was observed in the Yolindi area, which was distinguished by the formation of magnetite, pyrite, and medium-to-coarse-grained Fe-rich anhydrous calc-silicate minerals (e.g., andradite and augite). These minerals occurred in the endoskarn and proximal exoskarn zones. Magnetite was generated concurrently with pyrite during this phase (Figure 7). The occurrence of minerals, such as actinolite, epidote, scapolite, calcite, and chlorite pseudomorph, after garnet and pyroxene suggested that a retrograde stage occurred at lower temperatures and pressures. In addition, at this particular stage, the andradite–grossular intergrowth is associated with the hedenbergite. The aforementioned minerals are often formed in association with ore minerals, such as chalcopyrite, pyrite, specular hematite, galena, and sphalerite (Figure 7). Cerussite and malachite are characteristics of the supergene stage (Figure 7). This showed the process of metals moving and leaching from nearby areas, where primary metal sulfides break down and then turn into carbonates when the pH and redox conditions change.

Mineral	Prograde stage	Retrograde stage	Supergene stage
Andradite	████████████████████	████████████████	
Andradite-grossular		████████████████████	
Augite	████████████████████		
Hedenbergite		████████████████████	
Scapolite		████████████████████	
Epidote		████████████████████	
Chlorite		████████████████████	
Actinolite		████████████████████	
Calcite	████████████████████	████████████████	
Sericite		████████████████████	
Quartz	████████████████	████████████████████	
Magnetite	████████████████████	████████████████	
Spec. Hematite		████████████████████	
Chalcopyrite		████████████████████	
Bornite		████████████████████	
Pyrite	████████████████████	████████████████	
Galena		████████████████████	
Sphalerite		████████████████████	
Cerussite			████████████████
Malachite			████████████████
Goethite			████████████████

Figure 7. A paragenetic sequence of metamorphic, altered, and ore minerals in the Yolindi Fe-Cu skarn mineralization.

5.2. Fluid Inclusion Studies

5.2.1. Fluid Inclusion Petrography

The Yolindi Cu-Fe skarn mineralization exhibits a substantial prevalence of fluid inclusions, mostly found inside andradite, grossular, quartz, and calcite crystals. The FIs may be categorized into two phases of inclusion, namely liquid H₂O (L) and vapor H₂O (V), with one type being rich in liquid and the other type being rich in vapor, in accordance with the classifications of Roedder [32] and Van den Kerkhof and Hein [34]. Multiple instances have led to the identification of the primary and secondary fluid inclusions in these samples. On the other hand, the primary fluid inclusions exhibit a sub-rounded, elliptical, elongated, and irregular shape, and have a maximum size of 350 µm (Figure 8). The andradite minerals that occurred in the prograde proximal zone have FIs exhibiting sub-rounded, elliptical, and irregular forms with diameters ranging from 40 to 108 µm (Figure 8a,b). At room temperature, the vapor bubble typically fills around 15%–20% of the inclusion volume, as shown in Figure 8a,b. This mineral has vapor-rich inclusions that are presently sub-rounded and irregular in shape. These inclusions have diameters ranging from 65 to 102 µm and constitute 55%–65% of the volume of the vapor bubble at room temperature (Figure 8c). In contrast, the grossular, quartz, and calcite minerals generated during the retrograde proximal stage include liquid-rich L+V FIs. In grossular, quartz, and calcite minerals, these FIs have prismatic and irregular forms, with their diameters ranging from 16 to 154 µm, from 31 to 357 µm, and from 16 to 116 µm, respectively (Figure 8d–i). Furthermore, the vapor bubble accounts for 20%–25%, 9%–22%, and 10%–20% of the volume of FIs in grossular, quartz, and calcite FIs, respectively (Figure 8d–i). The quartz crystals in the intermediate retrograde zone include FIs with diameters ranging from 3 to 110 µm in diameter. These FIs are of the liquid-rich L+V type, as shown in Figure 8j. However, their morphologies exhibit irregularities, varying in diameter from 23 to 290 µm in the quartz minerals of the distal zone (Figure 8k,l).

5.2.2. Microthermometry Results

Extensive analysis was performed on a total of 119 fluid inclusions that occurred in andradite, grossular, quartz, and calcite minerals formed throughout the prograde and retrograde phases of skarn mineralization in the proximal, intermediate, and distal exoskarn zones. The main objective of this analysis was to determine the temperatures at which homogenization and freezing took place for each inclusion (Table 1). The eutectic temperatures (T_e) of liquid-rich and vapor-rich (L+V) fluid inclusions varied across various minerals (Table 1). The primary fluid inclusions of andradite, grossular, quartz, and calcite minerals from the proximal zone experienced T_e values ranging from -37.80 to -12.10 °C, from -8.80 to -1.60 °C, from -26.70 to -0.80 °C, and from -17.80 to -1.10 °C, respectively (Table 1). The T_e of the fluid inclusions (FIs) that were detected in quartz minerals from the intermediate and distal zones varied between -26.60 and -1.70 °C and between -8.60 and -1.90 °C, respectively (Table 1). These findings indicated the presence of a H₂O–NaCl system. In contrast, the final melting temperature (T_m) of the primary fluid inclusions in andradite, grossular, quartz, and calcite minerals from the proximal zone varied between -25.80 and -8.50 °C, between -5.30 and -0.40 °C, between -13.50 and -0.50 °C, and between -12.30 and -0.20 °C, respectively (Table 1). The T_m values of the FIs found in quartz minerals from the intermediate and distal zones ranged from -17.60 to -0.40 °C and from -3.40 to -0.90 °C, respectively (Table 1). The homogenization temperature (T_h) values of the primary FIs ranged from 359.00 to 412.20 °C (an average of 390.15 °C) for andradite minerals, from 280.10 to 372.60 °C (an average of 348.13 °C) for grossular minerals, from 256.00 to 394.30 °C (an average of 304.89 °C) for quartz minerals, and from 197.70 to 317.80 °C (an average of 280.45 °C) for calcite minerals (Table 1). The temperature range for the T_h of the FIs observed in quartz minerals from the intermediate and distal zones was between 299.80 and 370.00 °C, with an average temperature of 337.95 °C, and between 296.10 and 336.50 °C, with an average temperature of 319.47 °C, respectively (Table 1).

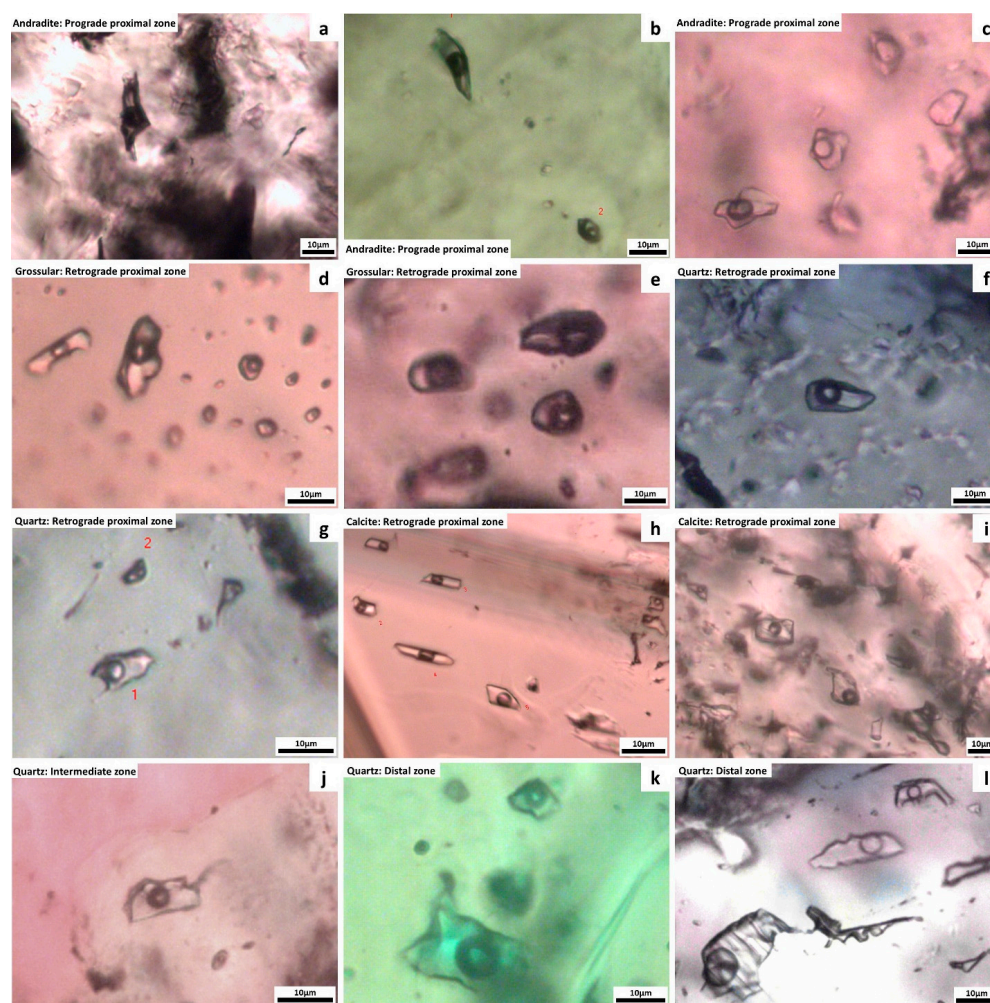


Figure 8. (a,b) Liquid-rich primary (liquid–vapor) fluid inclusions in andradite minerals from the prograde proximal exoskarn zone. (c) Vapor-rich primary (L+V) fluid inclusions with liquid-rich ones in andradite minerals from the prograde proximal exoskarn zone. (d,e) Liquid-rich primary (L+V) fluid inclusions in grossular minerals from the retrograde proximal exoskarn zone. (f,g) Liquid-rich primary (L+V) fluid inclusions in quartz minerals from the retrograde proximal exoskarn zone. (h,i) Liquid-rich primary (L+V) fluid inclusions in calcite minerals from the retrograde proximal exoskarn zone. (j) Liquid-rich primary (L+V) fluid inclusions in quartz minerals from the intermediate exoskarn zone. (k,l) Liquid-rich primary (L+V) fluid inclusions in quartz minerals from the distal exoskarn zone.

The salinities were calculated using the final ice melting temperatures (T_{m-ice}), as suggested by Darling [35], Archer [36], Bodnar [37], and Steele-MacInnis et al. [38], along with the utilization of the BULK computer software developed by Bakker [39] (Table 1). The salinities of the primary L+V FIs in the andradite minerals from the prograde proximal exoskarn zone varied from 12.28% to 26.07 wt.% NaCl equivalent, with an average of 20.27 wt.% NaCl equivalent (Table 1). In contrast, the grossular, quartz, and calcite minerals occurring in the retrograde proximal exoskarn zone had lower salinities in their fluid inclusions. The salinity of FIs in grossular minerals varied from 0.70 to 8.28 wt.% NaCl equivalent; in quartz, it ranged from 0.88 to 17.34 wt.% NaCl equivalent, and in calcite, it ranged from 0.35 to 16.24 wt.% NaCl equivalent (Table 1). The salinity range for FIs in quartz minerals was lower in the intermediate and distal zones compared to the proximal zones. It varied between 0.70 and 20.67 wt.% NaCl equivalent, with an average of 9.35 wt.% NaCl equivalent in the intermediate zone, and between 0.35 and 16.24 wt.% NaCl equivalent, with an average of 3.63 wt.% NaCl equivalent in the distal zone (Table 1). The total densities

of FIs were computed using the equation of state proposed by Zhang and Frantz [40]. The primary FIs in the andradite crystals from the prograde proximal zone have a density ranging from 0.69 to 0.91 g/cm³, with an average of 0.81 g/cm³. The densities of FIs in the grossular, quartz, and calcite minerals from the retrograde proximal zone range from 0.58 to 0.77 g/cm³ (with an average of 0.64 g/cm³), from 0.56 to 0.88 g/cm³ (with an average of 0.75 g/cm³), and from 0.71 to 0.89 g/cm³ (with an average of 0.78 g/cm³), respectively (Table 1). The overall densities of FIs in the quartz minerals from the intermediate and distal zones range from 0.65 to 0.86 g/cm³ and from 0.65 to 0.77 g/cm³, respectively (Table 1).

Table 1. Summary of microthermometric data and their calculations of andradite, grossular, quartz, and calcite minerals from the different skarn zones from the study area.

Mineral		Andradite	Grossular	Quartz	Quartz	Calcite	
Stage		Prograde	Retrograde	Retrograde	Retrograde	Retrograde	Retrograde
Zone		Proximal	Proximal	Proximal	Intermediate	Distal	Proximal
Inclusion type (primary)		L–V	L–V	L–V	L–V	L–V	L–V
Eutectic temperature (°C)	Interval	From −37.8 to −12.1	From −8.8 to −1.6	From −26.7 to −0.8	From −26.6 to −1.7	From −8.6 to −1.9	From −17.8 to −1.1
	n	10	13	17	20	12	24
	Avg	−24.1	−4.9	−7.0	−11.9	−4.7	−6.3
Tm-ice (°C)	Interval	From −25.8 to −8.5	From −5.3 to −0.4	From −13.5 to −0.5	From −17.6 to −0.4	From −3.4 to −0.9	From −12.3 to −0.2
	n	10	13	17	20	12	24
	Avg	−17.6	−1.8	−3.7	−6.7	−1.8	−2.3
Th-tot (°C)	Interval	From 359.0 to 412.2	From 280.1 to 372.6	From 256.0 to 394.3	From 299.8 to 370	From 296.1 to 336.5	From 197.7 to 317.8
	n	10	13	17	20	12	24
	Avg	390.2	348.1	304.9	337.9	319.5	280.4
Salinity %NaCl eq.	Interval	From 12.3 to 26.1	From 0.7 to 8.3	From 0.9 to 17.3	From 0.7 to 20.7	From 1.6 to 5.6	From 0.4 to 16.2
	n	10	13	17	20	12	24
	Avg	26.1	2.9	5.7	9.4	3.1	3.6
Density (g/cm ^{−3})	Interval	From 0.69 to 0.91	From 0.58 to 0.77	From 0.56 to 0.88	From 0.65 to 0.86	From 0.65 to 0.77	From 0.71 to 0.89
	n	10	13	17	20	12	24
	Avg	0.81	0.64	0.75	0.75	0.70	0.78
P _h (bar)	Interval	From 145.3 to 261.4	From 63.1 to 211.8	From 43.1 to 255.4	From 82.4 to 185.7	From 80.4 to 138.4	From 14.7 to 107.2
	n	10	13	17	20	12	24
	Avg	217.8	163.2	100.1	135.6	111.3	67.1

5.3. Stable Isotope Data

5.3.1. $\delta^{34}\text{S}$ Isotope of Sulfides

Stable isotope analysis was performed on 34 samples containing different sulfide minerals in order to ascertain the $\delta^{34}\text{S}$ isotopic composition (Table 2). The samples comprise six pyrite samples from the endoskarn zone, three pyrite samples and three chalcopyrite samples from the prograde proximal exoskarn zone, ten pyrite samples and three chalcopyrite samples from the retrograde proximal exoskarn zone, and seven pyrite samples and two chalcopyrite samples from the intermediate exoskarn zone (Table 2). All of these samples originated from the prograde and retrograde stages of mineralization, except for several pyrite minerals that formed alongside the Şaroluk granitic rock (see Figure 7). The $\delta^{34}\text{S}$ data of the two pyrite varieties from the endoskarn zone ranged from +0.27 to +0.57‰_{VCDT} and from −4.56 to −3.98‰_{VCDT}. The pyrite and chalcopyrite acquired from the prograde proximal exoskarn zone displayed a narrow range of sulfur isotopic values. Specifically,

the pyrite varied from -3.65 to $-0.17\text{‰}_{\text{VCDT}}$, while the chalcopyrite ranged from -4.23 to $-0.25\text{‰}_{\text{VCDT}}$ (Table 2). The sulfur isotopic values of pyrite and chalcopyrite in the retrograde proximal exoskarn zone ranged from -4.27 to $-2.59\text{‰}_{\text{VCDT}}$ for pyrite and from -3.84 to $-2.67\text{‰}_{\text{VCDT}}$ for chalcopyrite. In contrast, the pyrite and chalcopyrite detected in the intermediate exoskarn zone displayed a lower sulfur isotopic value. Specifically, the pyrite varied from -9.44 to $-5.46\text{‰}_{\text{VCDT}}$, while the chalcopyrite ranged from -8.88 to $-5.79\text{‰}_{\text{VCDT}}$ (Table 2). The $\delta^{34}\text{S}$ ratios of the ore-forming fluids were measured on the assumption that the sulfur included in these fluids was mostly in the form of H_2S . The calculations relied on fractionation equations established by Czamanske and Rye [41] and Ohmoto and Rye [42], which use the $\delta^{34}\text{S}$ values of sulfide minerals. The formational temperatures of the fluids were determined through the analysis of fluid inclusions. These analyses revealed that the average temperature of garnet minerals in the prograde zone was 390 °C , while the average temperature of the garnet, quartz, and calcite minerals in the retrograde zone was 323 °C . The measured $\delta^{34}\text{S}$ values of H_2S in the hydrothermal fluids varied between -5.47‰ and -0.34‰ , with an average of $-2.82\text{‰} \pm 0.18$, and between -5.39‰ and -1.08‰ , with an average of $-4.24\text{‰} \pm 0.18$, for the sulfides from the endoskarn and proximal zones, respectively. In contrast, these values ranged from -10.57‰ to -4.54‰ , with an average of $-7.54\text{‰} \pm 0.23$, for the sulfides from the intermediate zone. These values represent the overall sulfur isotopic composition of the magmatic–hydrothermal fluid ($\delta^{34}\text{S}_{\Sigma\text{S}}$), as shown in Table 2.

Table 2. Sulfur isotope values of sulfides from the Yolindi Cu-Fe Skarn mineralization.

Sample ID	Mineral	Host	Metamorphic Grade	Measured $\delta^{34}\text{S}$ (‰)	at T °C	$\delta^{34}\text{S}_{\text{H}_2\text{S}}$ Fluid (‰) ⁽³⁾	Error Range
BG-220A	Pyrite	Endoskarn		-4.56	$390^{(1)}$	-5.47	± 0.18
BG-220B	Pyrite	Endoskarn		-4.11	$390^{(1)}$	-5.02	± 0.18
BG-220C	Pyrite	Endoskarn		-3.98	$390^{(1)}$	-4.89	± 0.18
BG-85A	Pyrite	Endoskarn		0.57	$390^{(1)}$	-0.34	± 0.18
BG-85B	Pyrite	Endoskarn		0.27	$390^{(1)}$	-0.64	± 0.18
BG-87	Pyrite	Endoskarn		0.33	$390^{(1)}$	-0.58	± 0.18
BG-102	Pyrite	Proximal	Prograde	-3.65	$390^{(1)}$	-4.56	± 0.18
BG-33A	Pyrite	Proximal	Prograde	-0.17	$390^{(1)}$	-1.08	± 0.18
BG-103	Pyrite	Proximal	Prograde	-2.73	$390^{(1)}$	-3.64	± 0.18
BG-102	Chalcopyrite	Proximal	Prograde	-4.13	$390^{(1)}$	-5.04	± 0.18
BG-102A	Chalcopyrite	Proximal	Prograde	-4.23	$390^{(1)}$	-5.14	± 0.18
BG-33A	Chalcopyrite	Proximal	Prograde	-0.25	$390^{(1)}$	-1.16	± 0.18
BG-237F2	Pyrite	Proximal	Retrograde	-3.54	$323^{(2)}$	-4.67	± 0.23
BG-237F2	Pyrite	Proximal	Retrograde	-3.49	$323^{(2)}$	-4.62	± 0.23
BG-31A	Pyrite	Proximal	Retrograde	-2.59	$323^{(2)}$	-3.72	± 0.23
BG-44	Pyrite	Proximal	Retrograde	-3.7	$323^{(2)}$	-4.83	± 0.23
BG-44	Pyrite	Proximal	Retrograde	-3.9	$323^{(2)}$	-5.03	± 0.23
BSD-1	Pyrite	Proximal	Retrograde	-3.64	$323^{(2)}$	-4.76	± 0.23
BSD-10	Pyrite	Proximal	Retrograde	-3.48	$323^{(2)}$	-4.61	± 0.23
BSD-11	Pyrite	Proximal	Retrograde	-4.08	$323^{(2)}$	-5.21	± 0.23
BSD-11	Pyrite	Proximal	Retrograde	-4.26	$323^{(2)}$	-5.39	± 0.23
BSD-8	Pyrite	Proximal	Retrograde	-3.01	$323^{(2)}$	-4.14	± 0.23
BG-31A	Chalcopyrite	Proximal	Retrograde	-2.67	$323^{(2)}$	-3.80	± 0.23
BSD-10	Chalcopyrite	Proximal	Retrograde	-3.84	$323^{(2)}$	-4.96	± 0.23
BSD-8	Chalcopyrite	Proximal	Retrograde	-3.41	$323^{(2)}$	-4.54	± 0.23
BG-100	Pyrite	Intermediate	Retrograde	-9.44	$323^{(2)}$	-10.57	± 0.23
BG-101	Pyrite	Intermediate	Retrograde	-8.92	$323^{(2)}$	-10.05	± 0.23

Table 2. Cont.

Sample ID	Mineral	Host	Metamorphic Grade	Measured $\delta^{34}\text{S}$ (‰)	at T °C	$\delta^{34}\text{S}_{\text{H}_2\text{S}}$ Fluid (‰) ⁽³⁾	Error Range
BG-205	Pyrite	Intermediate	Retrograde	−5.72	323 ⁽²⁾	−6.85	± 0.23
BSS-4	Pyrite	Intermediate	Retrograde	−5.81	323 ⁽²⁾	−6.94	± 0.23
BSS-5	Pyrite	Intermediate	Retrograde	−5.46	323 ⁽²⁾	−6.58	± 0.23
BSS-6	Pyrite	Intermediate	Retrograde	−5.52	323 ⁽²⁾	−6.65	± 0.23
BSS-6	Pyrite	Intermediate	Retrograde	−5.59	323 ⁽²⁾	−6.72	± 0.23
BG-101	Chalcopyrite	Intermediate	Retrograde	−8.87	323 ⁽²⁾	−10.00	± 0.23
BG-205	Chalcopyrite	Intermediate	Retrograde	−5.79	323 ⁽²⁾	−6.92	± 0.23

⁽¹⁾ Based on the average homogenous temperature of the garnet minerals in the endoskarn and prograde zones;

⁽²⁾ Based on the average homogenous temperature of the garnet, quartz, and calcite minerals in the retrograde zone; ⁽³⁾ Calculated using the sulfur isotope fractionation equations outlined by Czamanske and Rye [41] and Ohmoto and Rye [42].

5.3.2. Carbon ($\delta^{13}\text{C}$) and Oxygen ($\delta^{18}\text{O}$) Isotope Studies

The carbon and oxygen isotopic compositions of calcite minerals obtained from marble ($n = 5$ samples), retrograde skarn ($n = 9$ samples), and prograde skarn ($n = 11$ samples) exhibited $\delta^{13}\text{C}$ values ranging from +1.89‰ VPDB to +2.23‰ VPDB (with an average of +2.06‰ VPDB), from −3.8‰ VPDB to −2.25‰ VPDB (with an average of −3.02‰ VPDB), and from −6.0‰ VPDB to +0.09‰ VPDB (with an average of −2.48‰ VPDB), respectively (Table 3). Additionally, the $\delta^{18}\text{O}$ values ranged from +21.61‰ VSMOW to +21.73‰ VSMOW (with an average of +21.67‰ VSMOW), from +0.94‰ VSMOW to +3.62‰ VSMOW (with an average of 2.45‰ VSMOW), and from +6.22‰ VSMOW to +18.14‰ VSMOW (with an average of +11.24‰ VSMOW) for the calcite minerals from marble, retrograde skarn, and prograde skarn, respectively (Table 3). Hence, the carbon isotope ratios ($\delta^{13}\text{C}$ values) of the samples generally exhibit a consistent pattern, showing little enrichment in the marble as compared to the prograde and retrograde calcite samples (Table 3). Nevertheless, the $\delta^{18}\text{O}$ values indicate a decrease in isotopic composition from the marble sample to the prograde and retrograde calcite samples. Moreover, the data provided relates to the declining carbon and oxygen isotopic compositions seen in calcite minerals throughout their transition from prograde skarn to retrograde skarn, which may be attributed to the elevated temperatures experienced in the prograde zone [43]. The fluid $\delta^{13}\text{C}_{\text{CO}_2}$ values calculated at 318 °C (the highest homogeneous temperatures (T_h (°C)) for calcite minerals based on the fluid inclusion data of calcite minerals) using the calcite–CO₂ fractionation equation established by Scheele and Hoefs [44] exhibited a range from −4.92‰ to −4.58‰ (with an average of −4.75‰), from −10.61‰ to −9.06‰ (with an average of −9.83‰) and from −9.45‰ to −6.72‰ (with an average of −8.47‰) for calcite collected from marble, retrograde skarn, and prograde skarn, respectively (Table 3). The fluid $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values were determined using the equation for oxygen isotopic fractionation of calcite–water developed by O’Neil et al. [45]. These values were calculated at the highest T_h of 318 °C (current fluid inclusion data) for calcite minerals. The range of values acquired for calcite from marble, retrograde skarn, and prograde skarn were from +20.88‰ VSMOW to +21.00‰ VSMOW, from 0.91‰ VSMOW to +3.49‰ VSMOW, and from +6.03‰ VSMOW to +17.57‰ VSMOW, respectively (Table 3). In Figure 9a, the diagram illustrates the relationship between $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$. The marble samples fell within the marine carbonate field, indicating their composition. On the other hand, the samples of prograde calcite were plotted in the fields of granites, mantle-derived carbonatite, and xenoliths, as well as the transitional area between these fields and marine carbonate. This suggested that the oxygen isotope ratio increased in prograde calcite samples as a consequence of the dissolution and decarbonization of Torosan formation marble at the contact of the Şaroluk intrusion (Figure 9a). In contrast, the calcite samples collected from the retrograde skarn exhibited a reduction in oxygen isotope values, which may be attributed to the influence of meteoric water (see Figure 9a). The isotopic fractionation factor was calculated using the calcite–water equation proposed by O’Neil et al. [45]. The mixing

curves for M–A were computed for several values of X (CO_2) and fluid rock ratios, including 0.01, 0.1, and 0.5, and 0.5, 2, 10, 40, 80, and 100, respectively (Figure 9b). The isotopic composition of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the prograde and retrograde stage skarn calcites of the Yolindi skarn mineralization exhibited a depletion pattern that aligns with the curves of 0.01, 0.1, and, rarely, 0.5 X (CO_2). Isotopic depletion was observed in both the oxygen and carbon isotopes. The fluid–rock ratios of skarn calcites during the prograde stage exhibited the highest variability, with their values ranging from 10 to 80. In contrast, the fluid–rock ratios pertaining to retrograde-stage skarn calcites have yet to be identified.

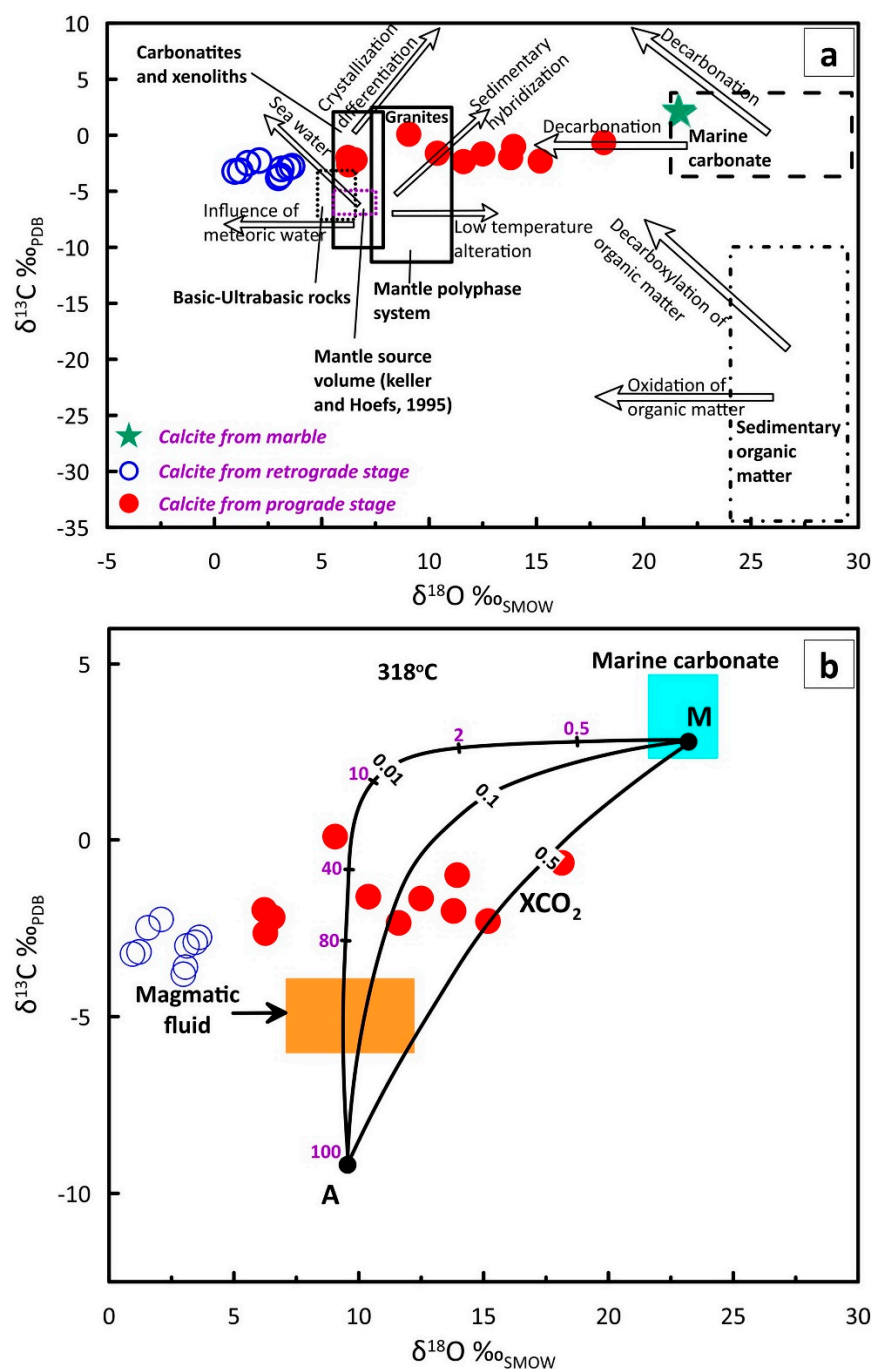


Figure 9. (a) $\delta^{13}\text{C}_{\text{PDB}}$ vs. $\delta^{18}\text{O}_{\text{SMOW}}$ binary diagram for calcites from marble, prograde, and retrograde skarn zones. These compositions were then compared with the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic compositions

of other rock types, as documented by Sheppard [46] and Hoefs [47]. (b) Plots of $\delta^{13}\text{C}_{\text{CO}_2}$ vs. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ isotopes of skarn calcites on the fluid–rock interaction model of Taylor [48], with curves generated for various $X(\text{CO}_2)$ and fluid–rock ratios of 0.01, 0.1, 0.5, 2, 10, 40, 80, and 100, respectively.

Table 3. Carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotope analyses of the calcite minerals from the different zones and rocks in the Yolindi Cu-Fe Skarn mineralization.

Sample ID	Zone	$\delta^{13}\text{C}$ (‰VPDB)	$\delta^{18}\text{O}$ (‰SMOW)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰) ⁽¹⁾	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰) ⁽²⁾
BG-41	Prograde	−1.98	6.22	−8.79	6.07
BG-237e	Prograde	−2.64	6.26	−9.45	6.11
BG-237d2	Prograde	−2.19	6.55	−9.00	6.39
BSS-9	Prograde	0.09	9.05	−6.72	8.84
BG-204b	Prograde	−1.61	10.38	−8.42	10.14
BG-62	Prograde	−1	13.94	−7.81	13.61
BG-39A	Prograde	−2.3	15.18	−9.11	14.82
BG-50	Prograde	−0.65	18.14	−7.46	17.70
BG-39b	Prograde	−2.35	11.60	−9.16	11.32
BG-39c	Prograde	−2.01	13.80	−8.82	13.47
BG-39d	Prograde	−1.66	12.50	−8.47	12.20
BSD-10	Retrograde	−3.23	0.94	−10.04	0.92
BSD-1	Retrograde	−3.17	1.20	−9.98	1.17
BG-35A	Retrograde	−2.49	1.56	−9.30	1.52
BSD-14	Retrograde	−2.25	2.09	−9.06	2.04
BSS-12	Retrograde	−3.8	2.97	−10.61	2.90
BSS-13	Retrograde	−3.6	3.06	−10.41	2.99
BSS-14	Retrograde	−3	3.12	−9.81	3.05
BSS-15	Retrograde	−2.9	3.45	−9.71	3.37
BSS-16	Retrograde	−2.76	3.62	−9.57	3.53
BG-304	Marble	1.89	21.73	−4.92	21.21
BG-305	Marble	2.23	21.61	−4.58	21.10
BG-306	Marble	1.96	21.71	−4.85	21.19
BG-307	Marble	2.07	21.67	−4.74	21.15
BG-308	Marble	2.16	21.63	−4.65	21.12

⁽¹⁾ Equation of carbon isotope for calcite, as discussed by Scheele and Hoefs [44]. ⁽²⁾ Equation of oxygen isotopic fractionation of calcite–water, as outlined by O’Neil et al. [45].

6. Discussion

6.1. Sulfur Isotopic Compositions and Their Geological Implications

The skarn deposits exhibit geological significance in relation to geodynamic settings, crustal recycling and metallogenesis, paleoenvironmental conditions, ancient hydrothermal systems, mineral resource potential, and regional metamorphic history [49,50]. Skarn deposits often form in fractures, hydrothermal systems, and igneous–carbonate contact zones [49]. Similar to earlier hydrothermal systems and pathways, metal-rich hydrothermal fluids mix with surrounding rocks to generate skarn deposits [50]. According to Ault and Kulp [51], the variation in $\delta^{34}\text{S}$ values within an ore deposit offers insights on the conditions under which it was generated, namely whether the deposits originated from fluids originating from a deep-seated magmatic source or from a more restricted source in the upper crust. Furthermore, it is crucial to recognize that various origins of sulfur in fluids responsible for ore formation encompass unique $\delta^{34}\text{S}$ values. Firstly, it is common for a mantle or magmatic source to have a $\delta^{34}\text{S}$ value within the range of $0 \pm 3\text{‰}$ [52]. McCuaig and Kerrich [53] stated that magmatic sources are formed through the dissolution or desulfidation of magmatic sulfides, having $\delta^{34}\text{S}$ values that range from 0‰ to $+9\text{‰}$. A seawater source has been identified via a $\delta^{34}\text{S}$ value of about $+20\text{‰}$ [53]. Furthermore, sedimentary rocks that have large negative $\delta^{34}\text{S}$ values exhibit a notable decrease in sulfur concentration, as stated by Rollinson [54].

The sulfur isotopic composition ($\delta^{34}\text{S}$) values obtained from the Yolindi Cu-Fe Skarn mineralization exhibited distinct variations. In the endoskarn zone, two varieties of pyrite

minerals occurred, with one having $\delta^{34}\text{S}$ values ranging from +0.27 to +0.57‰ $_{\text{VCDT}}$ and the other ranging from −4.56 to −3.98‰ $_{\text{VCDT}}$. Furthermore, the sulfide minerals in the exoskarn zones exhibited negative $\delta^{34}\text{S}$ values. The proximal zone showed a slight negative signature, ranging from −4.27 to −0.17‰ $_{\text{VCDT}}$ for pyrite and from −4.23 to −0.25‰ $_{\text{VCDT}}$ for chalcopyrite. On the other hand, the intermediate zone displayed significantly more negative values, ranging from −9.44 to −5.46‰ $_{\text{VCDT}}$ for pyrite and from −8.88 to −5.59‰ $_{\text{VCDT}}$ for chalcopyrite (see Table 2). These findings indicated the potential occurrence of a sulfur source that exhibits varying consistency and encompasses a number of characteristics with magmatic sources, as well as other sources, including sedimentary, biogenic, and/or metamorphic sources (Figure 10a). The $\delta^{34}\text{S}$ values of hydrogen sulfide (H_2S) in ore fluids for sulfide minerals in the endoskarn zone (from −5.47‰ to −0.34‰) and proximal zone (from −5.39‰ to −1.08‰) exhibited a slight negative pattern, which fell slightly within the range of sulfide minerals associated with the magmatic–hydrothermal signature described by Richards [55]. These findings indicated that the sulfur found in the pyrite and chalcopyrite minerals did not mainly originate from the Earth’s mantle. However, the $\delta^{34}\text{S}_{\text{fluid}}$ values still remained within the range of sulfur derived from magmatic sources [47]. The occurrence of very low (large and negative) $\delta^{34}\text{S}_{\text{fluid}}$ values in the intermediate zone (from −10.57‰ to −4.54‰) indicates the potential influence of negative $\delta^{34}\text{S}$ reservoirs, such as organic-rich sources, as detailed by Chambers [56] and Strauss [57], or similarities to metamorphic sulfide, as reported by Hutchison et al. [58] (Figure 10b). In summary, the sulfide-bearing fluid may have originated from either a magmatic–hydrothermal fluid, from the leaching process in igneous rocks, or from contributions from the organic-rich layers and/or metamorphic sources of the host metamorphic rocks of the Torasan formation. The fluctuation in sulfur isotope ratio from endoskarn to exoskarn zones and from prograde to retrograde zones in the Yolindi skarn mineralization may provide valuable insights into their physical and chemical evolution, as well as the processes involved in the processing of these deposits. Our previous article [4] discussed the transition from endoskarns to exoskarns in the Yolindi area, which indicates a spatial and temporal zonation in mineral chemistry within a skarn system. This transition is marked by different combinations of minerals, such as massive, un-zoned andradite and augite with magnetite in the endoskarn and zoned andradite in the proximal zone, indicating a prograde character [4]. Epidote, actinolite, and Cl-rich scapolite are newly formed hydrous minerals in the exoskarn intermediate and distal zones, as part of the retrograde system [4]. One instance of scapolite occurred in exoskarns, which had a greater concentration of chlorine. This indicates the presence of a hydrothermal fluid with a high NaCl content, possibly originating from the country metasediment rock of the Torasan formation [59]. The sulfur isotopic compositions at the first stage of skarn mineralization showed that the sulfur originated from a magmatic source. The sulfur isotopic compositions ($\delta^{34}\text{S}$) varied from 0.27‰ to 0.57‰ and from −4.56‰ to −0.17‰ in the endoskarn zone (see Table 2 and Figure 10). As the system evolved from the prograde stage to the retrograde stage, the ($\delta^{34}\text{S}$) values changed from −9.44‰ to −2.59‰ (see Table 2 and Figure 10). During this transition, there was a gradual decrease in the $\delta^{18}\text{O}$ fluid values from 6.0‰ to 17.6‰ in the prograde zone and from 0.9‰ to 3.5‰ in the retrograde zone (see Table 3). This suggested that there was an increase in mixing with meteoric water [60]. Figures 10 and 11 depict the typical ranges of sulfur isotopic compositions displayed under different geological settings. The $\delta^{34}\text{S}$ values of sulfide minerals reported in several skarn deposits in Turkey and worldwide displayed a broad range of values, all of which were within the range of $\delta^{34}\text{S}$ values seen in granitic rocks (Figure 10a). When differentiating between ore deposits from sedimentary and igneous settings, it is important to approach the use of sulfur isotopes with caution due to the substantial overlap seen in $\delta^{34}\text{S}$ values (Figure 10a). This occurrence may be attributed to the significant deposition of sulfide and sulfate minerals from the hydrothermal fluids during the mineralization process [61]. Figure 11 revealed that the studied Yolindi Cu-Fe skarn mineralization shares similarities with various other deposits, namely the Çataltepe deposits in Turkey [62], Fırıncıkdere in Kalkın in Turkey [63], Mazraeh in NW Iran [60],

Ditto in Japan [64], Shenshan in NE China [65], and Velardeña in Mexico [66] (Figure 11). These deposits exhibited a significant reduction in $\delta^{34}\text{S}$, indicating a strong link between the sulfur isotopic composition of rock sulfur and ore sulfur in the magnetite series of granitoids. This also suggested that they may have developed via contact metasomatism, with their light sulfur likely originating from biogenic sulfur present in the sedimentary rocks [64,67].

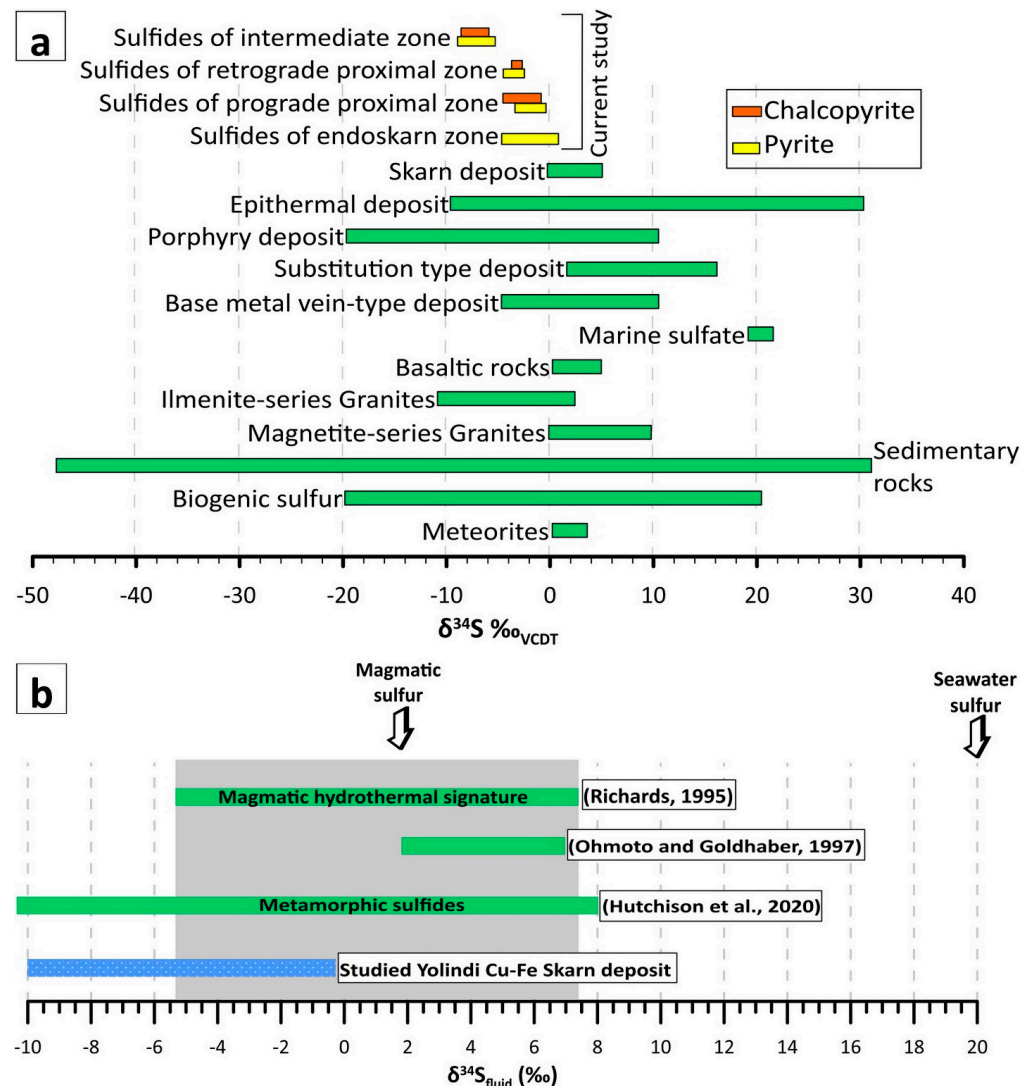


Figure 10. (a) $\delta^{34}\text{S}$ values of various geologic reservoirs, as reported by Seal [68], while skarn deposits were detailed by Taylor [69]. (b) $\delta^{34}\text{S}_{\text{fluid}}$ values of the Yolindi skarn mineralization and their comparison with the magmatic–hydrothermal deposits from Richards [55] and Ohmoto and Goldhaber [70] and metamorphic sulfide from Hutchison et al. [58].

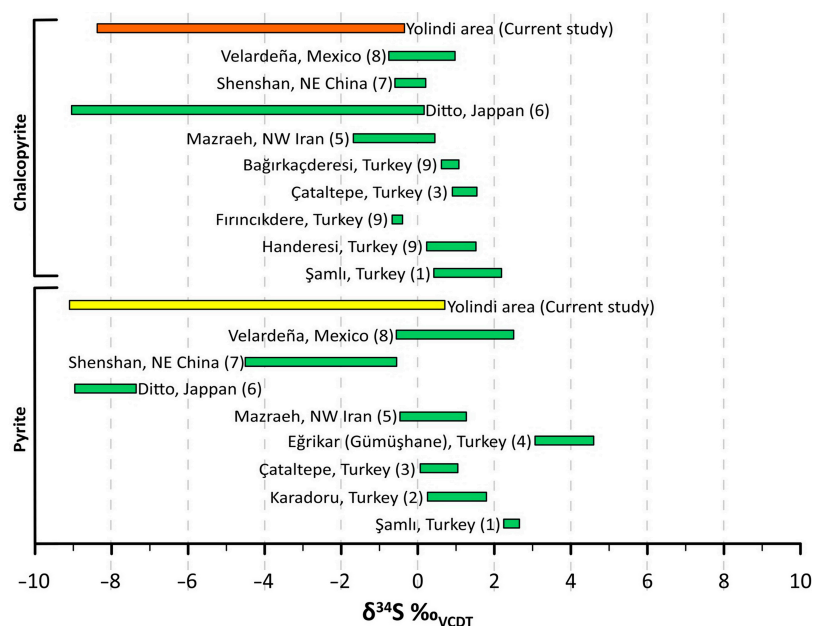


Figure 11. Sulfur isotopic composition diagram for sulfides from Yolindi area in the Biga Peninsula. Compilation of S isotope data: (1) Şamlı, Turkey [71]; (2) Karadoru, Turkey [72]; (3) Çataltepe, Turkey [62]; (4) Eğrikar (Gümüşhane), Turkey [73]; (5) Mazraeh, NW Iran [60]; (6) Ditto, Japan [64]; (7) Shenshan, NE China [65]; (8) Velardeña, Mexico [66]; and (9) Handeresi-Bağırkaçderesi-Fırıncıkdere in Kalkım, Turkey [63].

6.2. Source of Carbon

The $\delta^{13}\text{C}/\delta^{12}\text{C}$ isotope ratio has often been used for the purposes of determining the source of carbon dioxide (CO_2) derived from gas associated with magmatic–hydrothermal systems. In addition, it can be inferred that the computed $\delta^{13}\text{C}_{\text{CO}_2}$ is almost considered the $\delta^{13}\text{C}_{\Sigma\text{C}}$ of the fluid [74]. This ratio is a valuable tool for distinguishing between various potential sources of fluid. These sources include: (i) gases originating from the Earth’s mantle, which typically have $\delta^{13}\text{C}_{\text{CO}_2}$ values ranging from -7‰ to -3‰ VPDB [75,76]; (ii) the degradation of organic matter, which often produces significantly negative $\delta^{13}\text{C}_{\text{CO}_2}$ values ($\leq -20\text{‰}$ VPDB; Hoefs [47] and O’Leary [77]); and (iii) thermal metamorphic processes associated with the decomposition of limestone, which are typically characterized by CO_2 with isotopically enriched values ($\delta^{13}\text{C}_{\text{CO}_2}$: $>0 \pm 1\text{‰}$ VPDB; Sano and Marty [78], Tedesco and Scarsi [79], Minissale [80] and Clark [81]). Typically, the presence of intermediate $\delta^{13}\text{C}_{\text{CO}_2}$ values has often been attributed to the amalgamation of carbon dioxide derived from several sources. Nevertheless, several studies have provided evidence indicating that the carbon isotopic composition of various gases is subjected to significant alterations due to the secondary processes of isotope fractionation. These processes include the interaction between gas and water, as demonstrated by Weinlich [82], Gilfillan et al. [83], Darrah et al. [84], and Güleç and Hilton [85]. Additionally, the precipitation or dissolution of carbonate minerals has been shown to have an impact on carbon isotopes in gases, as evidenced by Ohwada et al. [86], Barry et al. [87], and Venturi et al. [88]. Hence, it is important to be careful in interpreting $\delta^{13}\text{C}_{\text{CO}_2}$ data, especially for gases derived from regions with restricted geological constraints [89]. The measured $\delta^{13}\text{C}_{\text{CO}_2}$ values of prograde calcite varied between -9.45 and -6.72‰ VPDB and demonstrated conformity with a magmatic source derived from the Earth’s mantle, with an influence from the thermal degradation of organic materials (Figure 12a). In contrast, the $\delta^{13}\text{C}_{\text{CO}_2}$ values of retrograde calcite exhibited a range from -10.61 to -9.06‰ VPDB, indicating that the CO_2 was solely derived by the thermal degradation of organic matter (Figure 12a).

6.3. Calcite-Forming Fluid Sources

Hydrothermal fluids from various sources have distinct carbon–oxygen isotopic compositions, as shown by Demény and Harangi [90], Demény et al. [91], Zheng and Chen [92], and Zhou et al. [93]. Particularly, carbon dioxide (CO_2) originating from the mantle or igneous carbonate sources displays a variety of isotopic compositions. More precisely, it has a $\delta^{13}\text{C}_{\text{PDB}}$ value that varies between -8‰ and -4‰ , and a $\delta^{18}\text{O}_{\text{SMOW}}$ value that ranges from 6‰ to 10‰ [91,94]. However, CO_2 that comes from marine carbonate sources has distinct isotopic characteristics varying between -4‰ and 4‰ , whereas the $\delta^{18}\text{O}_{\text{SMOW}}$ value ranges from 20‰ to 30‰ [95]. In addition, CO_2 originating from sedimentary organic matter has unique isotopic compositions, having $\delta^{13}\text{C}_{\text{PDB}}$ values ranging from -30‰ to -15‰ , whereas its $\delta^{18}\text{O}_{\text{SMOW}}$ value ranges from 24‰ to 30‰ [47]. Furthermore, the carbon isotopic composition of the hydrothermal fluids, when paired with the oxygen isotopic composition, offers more insight into the origins of the fluid in the hydrothermal system. However, the carbon isotope signature of the water source remained rather ambiguous. The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ data in the Yolindi area exhibited a wide range of variability. These values for calcite from prograde skarns varied from $+6.03\text{‰}$ to $+17.57\text{‰}$, and for calcite from retrograde skarns, they ranged from $+0.91\text{‰}$ to $+3.49\text{‰}$. These findings indicate that the hydrothermal fluid that caused the formation of calcite crystals in the prograde skarn zone is a mixture of metamorphic and magmatic sources, perhaps originating from mantle or igneous origins (Figure 12b). The calcite minerals in the retrograde skarn zone were formed via the activity of hydrothermal fluids originating from meteoric sources, as shown in Figure 12b.

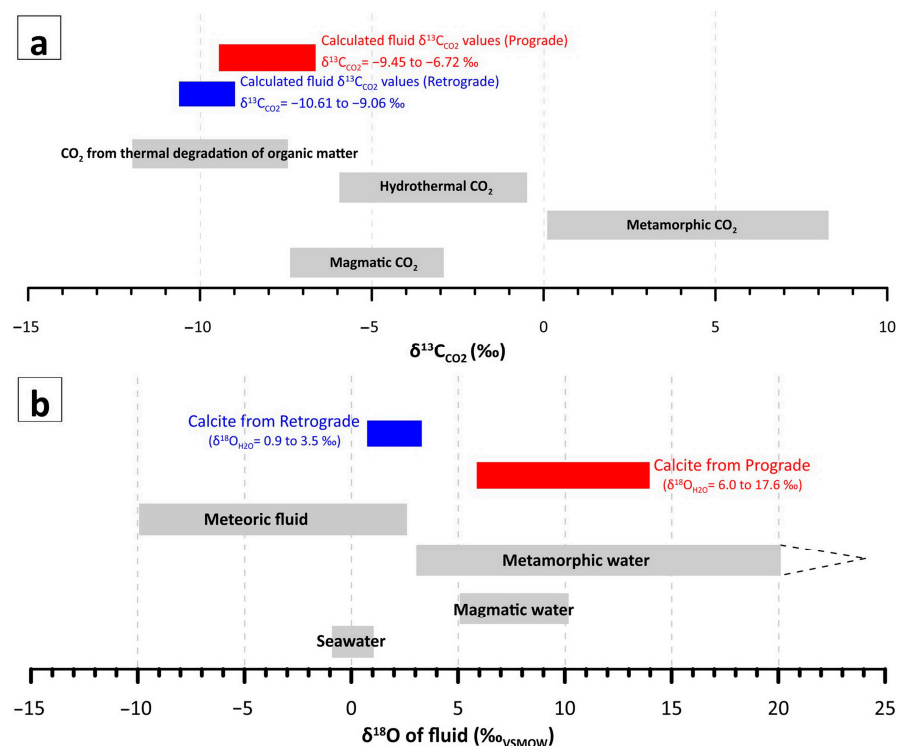


Figure 12. (a) The $\delta^{13}\text{C}_{\text{CO}_2}$ values of calcite minerals from prograde skarn and retrograde skarn were compared to the natural $\delta^{13}\text{C}_{\text{CO}_2}$ values from different sources, as reported by Schidlowski [96] and Planavsky et al. [97]. (b) The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of calcite minerals from prograde skarn and retrograde skarn were compared to the natural $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values from different sources, as detailed by Sheppard [98] and Rollinson and Pease [99].

6.4. Composition of Hydrothermal Solutions

Eutectic temperatures (T_e) have been ascertained for different types and phases of inclusions occurring in andradite, grossular, quartz, and calcite minerals. The eutectic temperatures of the prograde proximal stage inclusions in andradite ranged from -37.80 to -12.10 °C. The temperatures mentioned are associated with the mixing of H_2O – CaCl_2 – MgCl_2 – NaCl salt solutions [33], rather than being specific to individual phases (Figure 13). Nevertheless, the eutectic temperatures of the retrograde stage inclusions of grossular, quartz, and calcite minerals in the proximal, intermediate, and distal zones were found to be frequently comparable with the eutectic temperature of the H_2O – NaCl system [33] (Figure 13). Considering these eutectic temperatures at all stages, the composition of the prograde early phases of inclusions was characterized by a combination of CaCl_2 - and MgCl_2 -dominated systems [33]. CaCl_2 and MgCl_2 are the main components of hydrothermal fluids, as stated by Roedder [32]. The salinity and temperature of this particular stage of inclusion exhibited greater values compared to the retrograde phases. The existence of CaCl_2 and MgCl_2 indicates a direct or indirect interaction with either hydrothermal fluid or marine carbonate in the nearby area [100,101]. The carbonaceous rocks that were found in the Torasan formation within the skarn contacts are the only plausible origin for the first-stage inclusions bearing CaCl_2 and MgCl_2 during the prograde stage. Thus, the existence of CaCl_2 and MgCl_2 in the fluid inclusions can be attributed to a variety of factors, including the evolution of hydrothermal systems, temperature and salinity fluctuations, fluid immiscibility (or boiling), and the presence of distinct types of fluid inclusions, such as liquid-rich and vapor-rich inclusions, in this stage [102,103]. Later on, it was discovered that the retrograde stage inclusions were mostly composed of NaCl , based on the very similar eutectic temperatures of the NaCl – H_2O system [33]. The transition from a composition mostly consisting of CaCl_2 and MgCl_2 to one dominated by NaCl in the fluid inclusions indicates that there were significant interactions between the hydrothermal solutions and carbonaceous host rocks during the first stages of skarnification. During the retrograde phase, a reduction in the interaction between the hydrothermal fluids and carbonates may have resulted in alterations that led to compositions dominated by NaCl .

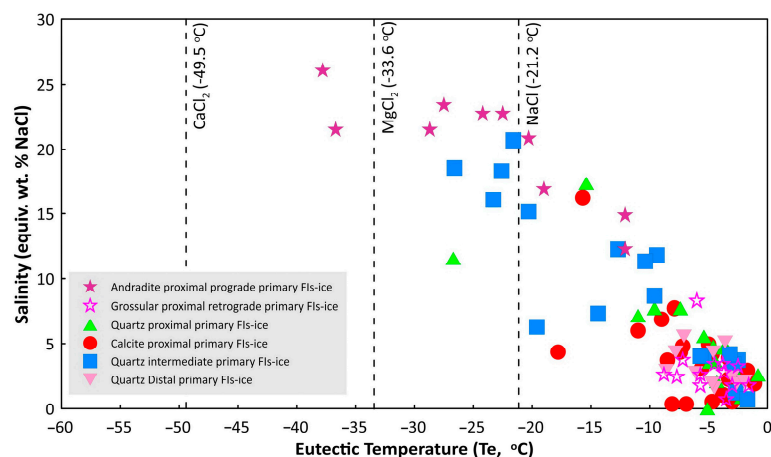


Figure 13. Comparing the measured eutectic temperatures of fluid inclusions from various mineral phases at different stages with the eutectic temperatures of certain salt solutions according to Shepherd et al. [33] and Wilkinson [104].

6.5. Evolution of Ore-Forming Fluids

The prograde-stage inclusions had higher salinity, reaching up to 26.07 wt.% NaCl equivalent, and higher T_h temperatures, reaching up to 412.20 °C (Figure 14). In contrast, the fluid inclusions during the retrograde stage exhibited reduced salinity and T_h temperatures. The salinity content of the minerals formed during the retrograde stage (i.e., grossular, quartz, and calcite) dropped as the temperature of the fluid inclusions decreased

(Figure 14). This decrease in salinity was ascribed to the amalgamation of meteoric water and hydrothermal solutions [104], as well as the interaction of the solution with the organic material within the host Torasan formation. The results unequivocally show that the salinity content of hydrothermal solutions was higher during the first phase (prograde) of skarn formation due to the interaction between the fluids originating from magma and carbonaceous rock units of the Torasan formation. During the later stages (retrograde), the addition of meteoric water resulted in a decrease in salinity levels and a reduction in fluid temperatures.

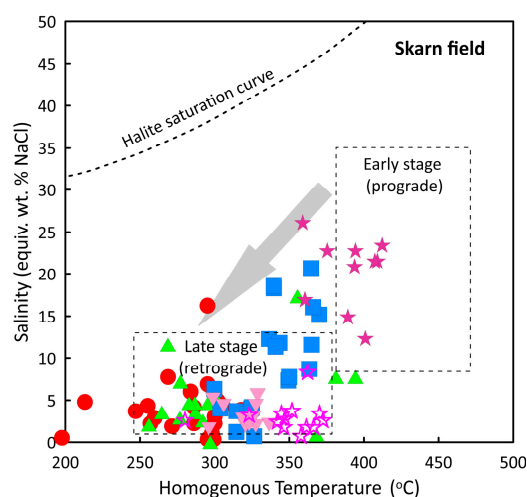


Figure 14. Salinity vs. total homogenization temperature plot of the fluid inclusions [105], the skarn field after Roedder [32], showing the fluid evolution in the Yolindi Cu-Fe skarn mineralization. The symbols are shown in Figure 13.

The ore-forming fluid evolution of the Yolindi Cu-Fe skarn mineralization began with the crystallization and cooling of the Şaroluk quartz monzonite and granodiorite in the shallow crust. The early skarn stage (prograde) is characterized by relatively moderate-to-high salinities, reaching up to 26 wt.% NaCl equivalents. These salinities were believed to be the result of a magmatic fluid component that underwent boiling [106] from the crystallizing Şaroluk quartz monzonite–granodiorite parental magma. It has been widely reported that the Şaroluk intrusion, which formed at shallow depths, contains volatile-rich magmas. This has been supported by various studies [27,107–111]. The presence of these magmas promotes the direct release of metalliferous and highly saline aqueous fluids [55]. In this particular setting, the first fluids that separate will possess salinities of moderate levels (6–8 wt.% NaCl equivalent; Bodnar) [106]. During the process of crystallization, the concentration of chlorine increases in the molten substance. This causes the fluids that are still separating to have progressively increasing levels of salinity. The andradite minerals in this early-stage (prograde) proximal exoskarn zone contain liquid-rich and vapor-rich two-phase (L+V) aqueous inclusions. These inclusions indicate that fluid boiling occurred during this early stage, resulting from the boiling process of the initial supercritical fluid. This fluid boiling was found to be directly associated with the earlier skarn stage (Figure 15). Therefore, the magnetite deposition in the proximal zone during the prograde stage was most likely a result of boiling, along with a reduction in temperature and/or pressure of the hydrothermal fluids.

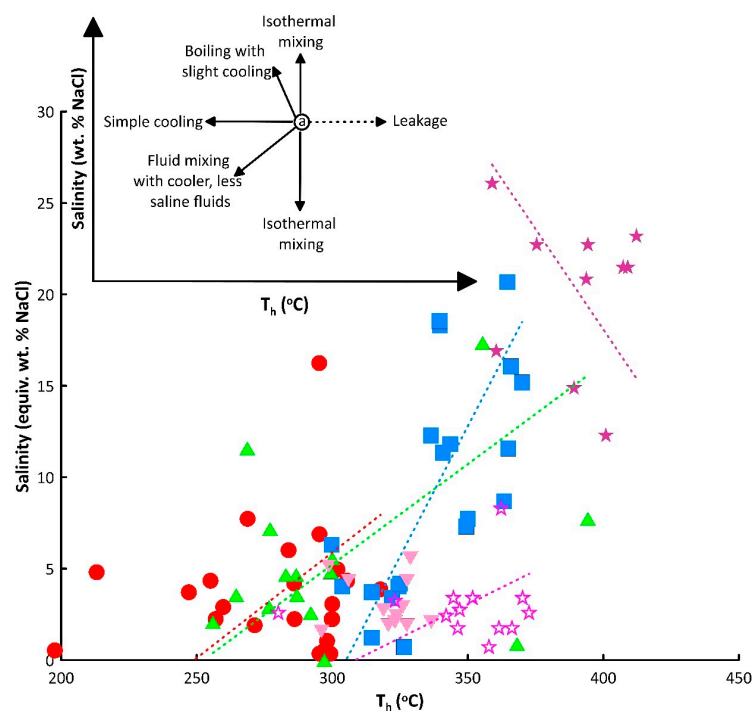


Figure 15. Homogenization temperature (T_h °C) and salinity (wt.% NaCl) diagram for the Yolindi Cu-Fe skarn mineralization [104]. Shepherd et al. [33] modified the figure inset to depict temperature–salinity trends or fluid evolution pathways deriving from various geological events. The dotted lines indicate the line graphs for each sample type. The symbols are shown in Figure 13.

On the other hand, the cooling and reduction in pressure and salinity, as well as changes in fluid composition, during the transition from the prograde stage to the retrograde stage of skarnification can be elucidated via various processes [112]: (1) the infiltration of meteoric water and its mixing with a prevailing magmatic fluid; (2) the addition of basinal fluids from the nearby sedimentary host rocks; and/or (3) the liberation of CaCl_2 during the creation of calc-silicate minerals and skarn [113]. Several porphyry and skarn systems, such as those described by Roedder [32] and Lai et al. [114], have shown similar tendencies. The fluids responsible for forming ores during the later stage (retrograde) in the proximal, intermediate, and distal exoskarn zones at the Yolindi area were found to be colder and more diluted compared to the earlier stage. This is evident from the obvious linear patterns shown in Figure 15, indicating that the influence of mixing with meteoric water is considerable [1]. The ongoing influx and mixture of meteoric water, which is relatively cold and has low salinity, resulted in ore-forming fluids with a moderate–low temperature and moderate–low salinity. The occurrence of relatively higher iron grades, associated with retrograde skarn formations, suggested that magnetite and specular hematite were formed concurrently during this stage of skarn mineralization. This is in contrast to the earlier phases, where only magnetite was formed as the initial iron oxide. The principal cause of iron deposition seems to be the combination of magmatic-dominated fluids from the crystallizing Şaroluk intrusion with cooler fluids emanating from the surface. The sulfide-rich mineralization deposition during the latter phase of the retrograde stage in the intermediate and distal zones indicated that it may have taken place under skarns to porphyry–epithermal transitional conditions (?) e.g., Bouabdellah et al. [112]. The probable explanation of this phenomenon may be attributed to a drop in temperature, pressure, and salinity, together with the occurrence of vuggy quartz and the substitution of lattice-bladed calcite with quartz. The mineralization originated from fluids with a salinity of less than 15 wt.% NaCl equivalent. The formation occurred at temperatures ranging from 390 to 197 °C and pressures below 250 bars [112]. Therefore, it is very likely that the cooling and

boiling of these fluids, together with the majority of fluid mixing, significantly influenced the creation of iron and sulfide minerals.

7. Conclusions

This comprehensive study of the Yolindi Cu-Fe skarn mineralization represents a significant advancement in understanding the complex interplay of geological processes responsible for skarn formation and mineralization. Utilizing a multidisciplinary approach, combining microthermometry of fluid inclusions with isotopic analysis ($\delta^{34}\text{S}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$), this study has elucidated the physiochemical conditions and fluid evolution within this skarn mineralization process. The findings highlight the significance of magmatic impacts, meteoric water interactions, and the role of the host rock matrix in shaping the mineralization process.

The isotopic data, particularly sulfur isotopes in sulfide minerals and carbon and oxygen isotopes in calcite, have provided key insights into the sources of sulfur and the composition and temperature of fluid–rock interactions. The variable $\delta^{34}\text{S}$ levels across different skarn zones highlight the diverse sulfur origins, ranging from magmatic impacts in endoskarn zones to organic-rich and potentially metamorphic origins in exoskarn zones. This isotopic variability reflects the complex dynamics of sulfur incorporation into the skarn system. Additionally, carbon and oxygen isotope evidence from calcites revealed a significant shift in fluid sources and interactions, transitioning from a dominantly magmatic CO_2 source in the prograde skarn to predominantly meteoric water and organic material during the retrograde stage.

The fluid inclusion studies further complemented these findings, delineating a clear temporal and compositional transition of the hydrothermal fluids. The early prograde stage was characterized by high salinity and boiling magmatic fluids, indicative of intense interactions with carbonaceous rocks. The retrograde phase, marked by lower salinity and temperatures, signified the increasing influence of meteoric water and organic-rich host rocks, culminating in a complex mineralization process. This transition from high-salinity, magmatic-dominated fluids to more diluted compositions reflects the intricate interplay between deep magmatic processes and surface water influences in the formation of the Yolindi skarn mineralization.

In summary, the Yolindi Cu-Fe skarn mineralization offers a quintessential example of skarn formation, where the convergence of magmatic and meteoric fluids, coupled with the geochemical characteristics of the host rock, plays a pivotal role in mineralization. The achievements of this study lie in its detailed characterization of these interactions and their influence on ore-forming processes, contributing to a deeper understanding of the formation and evolution of skarn deposits.

Author Contributions: Conceptualization, M.K. (Mustafa Kaya), M.K. (Mustafa Kumral), C.Y. and A.A.; methodology, M.K. (Mustafa Kaya) and A.A.; software, M.K. (Mustafa Kaya) and A.A.; validation, M.K. (Mustafa Kaya) and A.A.; formal analysis, M.K. (Mustafa Kaya), M.K. (Mustafa Kumral) and A.A.; investigation, M.K. (Mustafa Kaya) and A.A.; resources, M.K. (Mustafa Kaya) and A.A.; data curation, M.K. (Mustafa Kaya) and A.A.; writing—original draft preparation, M.K. (Mustafa Kaya) and A.A.; writing—review and editing, M.K. (Mustafa Kaya), M.K. (Mustafa Kumral) and A.A.; visualization, M.K. (Mustafa Kaya) and A.A.; supervision, M.K. (Mustafa Kumral) and A.A. All authors took part in the fieldwork. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data are available in Tables 1–3.

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