

Article

Genesis and Evolution of the Yolindi Cu-Fe Skarn Deposit in the Biga Peninsula (NW Turkey): Insights from Genetic Relationships with Calc-Alkaline Magmatic Activity

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Abstract: The current work investigates the impact of magmatic fluids and metasomatic processes on the Yolindi Cu-Fe skarn deposit in the Biga Peninsula, Turkey. It traces the stages of skarn evolution, from prograde to retrograde alterations, and investigates findings within a broader geological, mineralogical, and geochemical framework. Additionally, it assesses the evolutionary history of the Yolindi deposit in relation to calc-alkaline magmatic activity in an island-arc environment and compares its mineral compositions and genesis with other global and regional Cu-Fe skarn deposits. The Yolindi Cu-Fe skarn deposit in the Biga Peninsula was formed by the intrusion of Şaroluk quartz monzonite pluton into Upper Paleozoic Torasan Formation rocks such as phyllite, schists, hornfels, marble, and serpentinites. During skarnification, reactions between the magmatic fluids from the Şaroluk quartz monzonite pluton and the Torasan Formation produced skarn minerals associated with metals such as Fe and Cu. Initially, these reactions formed prograde skarn minerals such as augite-rich pyroxenes and andradite garnets with magnetite and pyrite. As the system cooled, these initial minerals underwent retrograde alteration, leading to the formation of minerals such as epidote, actinolite, and chlorite, as well as other copper and iron minerals including chalcopyrite, bornite, secondary magnetite, and specular hematite. Therefore, four main stages influenced the formation of the Yolindi Cu-Fe deposit: metamorphic bimetasomatic, prograde metasomatic, and retrograde metasomatic stages. Later, oxidation and weathering resulted in supergene minerals such as cerussite, malachite, and goethite, which serve as examples of the post-metamorphic stage. The mineralogical shifts, such as the andradite–grossular transition, reflect changing hydrothermal fluid compositions and characteristics due to the addition of meteoric fluids. Importantly, the formation of magnetite after garnet and clinopyroxene during the retrograde stage is evidenced by magnetite crystals within garnet. The mineral associations of the Yolindi Cu-Fe skarn deposit align with the global skarn deposits and specific Turkish skarns (e.g., Ayazmant Fe-Cu and Evciler Cu-Au skarn deposits). The Yolindi Cu-Fe skarn deposit, in association with ore-bearing solutions having magmatic origins, developed in an island-arc setting.

Keywords: EPMA data; geochemistry; mass balance calculation; Yolindi Cu-Fe skarn deposit; Şaroluk pluton; Biga Peninsula; NW Turkey



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1. Introduction

As a result of changes in fluid composition, pressure, and temperature, a skarn system frequently displays zonal alterations [1]. These zonal patterns may run concentrically (outward from the igneous intrusion) or perpendicular to the intrusion/carbonate-rich rock and limestone contact [1]. Mineral assemblages are a common way to express these zones. Based on their proximity to the caused intrusion, Ray and Webster [2] and Meinert [3]

divided skarns into endoskarns and exoskarns. An endoskarn forms within the intrusive body itself, typically in its outer regions. It is produced by the interaction of the igneous body and the magmatic fluid [1]. Even while it is frequently less widespread than exoskarns, it can, nonetheless, contain sizable mineral reserves. Garnet, pyroxene, quartz, and ore minerals including magnetite, pyrite, chalcopyrite, and bornite are frequently found among the minerals found in endoskarns, along with sphalerite and galena on occasion [1]. However, an exoskarn forms around the intrusive body in the country rock. It frequently contains garnet, pyroxene, and wollastonite, as well as ore minerals such as chalcopyrite, magnetite, and maybe sphalerite and galena, and develops due to metasomatism caused by the magmatic fluids that are heated by the intrusive body [1]. These minerals can exhibit a specific zoning pattern that reflects variations in the fluid composition and temperature. For instance, garnet may predominate in the exoskarn's outermost regions (showing higher temperature circumstances), whereas epidote and other silicates might become more prevalent as one moves into the interior (indicating lower temperature conditions) [1]. In this context, Meinert [4] divided these zonal patterns into three subzones based on how close they are to the intrusive body: proximal, intermediate, and distal zones.

Skarn deposits, which are predominantly classified as Fe-skarns and Cu-skarns, are a significant mineral deposit located on the Biga Peninsula of Turkey (Figure 1). Fe-skarns are the most abundant type of skarn deposit in western Anatolia. They arise when plutonic rocks such as granodiorite, monzodiorite, quartz diorite, or diorite intrusions emplace into metamorphosed sedimentary to volcanosedimentary rocks [5]. These skarns frequently co-generate with porphyry Cu deposits or epithermal Au deposits. This suggests that the Fe-skarns in the Biga Peninsula are an outcome of the broader magmatic–hydrothermal systems developed in high-level porphyry settings [5]. They are distinguished by economically valuable Cu mineralization that occurs as veins or irregular pockets that extend across magnetite ore bodies. These deposits are related to the Oligocene to Lower Miocene granitoids, particularly diorite and monzodiorite dike-like bodies close to the intersection of graphitic recrystallized limestone [5]. The deposits, including Uskufcu, Demirtepe, Evciler, and Bakirlik, frequently coexist with high-level porphyry systems as well (Figure 1). The Cu-skarns in the Biga Peninsula are made up of garnet–pyroxene and wollastonite–garnet skarns in endoskarn zones and wollastonite–garnet skarns in exoskarn zones [5]. However, Fe-skarns in the Biga Peninsula include magnetite, phlogopite, and actinolite and exhibit the alteration of magnetite to hematite, leading to supergene copper enrichment. There is also economically significant gold mineralization in the altered prograde skarns of certain deposits; this mineralization appears as magnetite and chalcopyrite lenses or pockets [5]. The region also has Mo-skarns, yet these are rather less prevalent than Fe-skarns and are typically regarded as being unprofitable. These Mo-skarns frequently include W and Cu mineralization and are mostly found in the regions of Soğucak, Sofular, Ayvalik, and Çakiroba. Their grade ranges from 0.1% to 0.6% Mo. These diverse skarns demonstrate how the Biga Peninsula is mineral-rich and how important it is for mining exploration and development [5].

The Yolindi area has previously been studied geologically and petrologically in general [6–10] but without a special focus on the genesis of the confined Cu-Fe skarn mineralization. As a result, this study discusses the genesis and formation of the Yolindi Cu-Fe skarn deposit in the Biga Peninsula, emphasizing the relationship between the intrusion of Şaroluk granitoid rocks and the nearby Torasan Formation rocks. It also traces the metasomatic processes that lead to skarn mineralogy, highlighting the role of magmatic fluids and their influence on mineral formation, alteration, and metal associations, particularly with copper and iron. It also seeks to identify and delineate the various stages of skarn evolution, from prograde to retrograde alterations. Furthermore, it attempts to contextualize the findings within a broader framework by comparing the mineralogy and genesis of the Yolindi deposit to other global and regional Cu-Fe skarn deposits and assessing their evolutionary history in relation to magmatic activity, particularly in an island-arc environment. This will be accomplished by conducting comprehensive field, petrographic, mineralogical, and

geochemical investigations of the newly formed skarn minerals, alterations, and associated mineralization of the Yolindi deposit. Geochemical studies of ore-related hydrothermal alterations were performed to examine the chemical exchanges between host rocks and hydrothermal ore fluids. The P-T conditions of ore deposition are approximated by utilizing the mineral chemistry of skarn, alteration, and ore minerals.

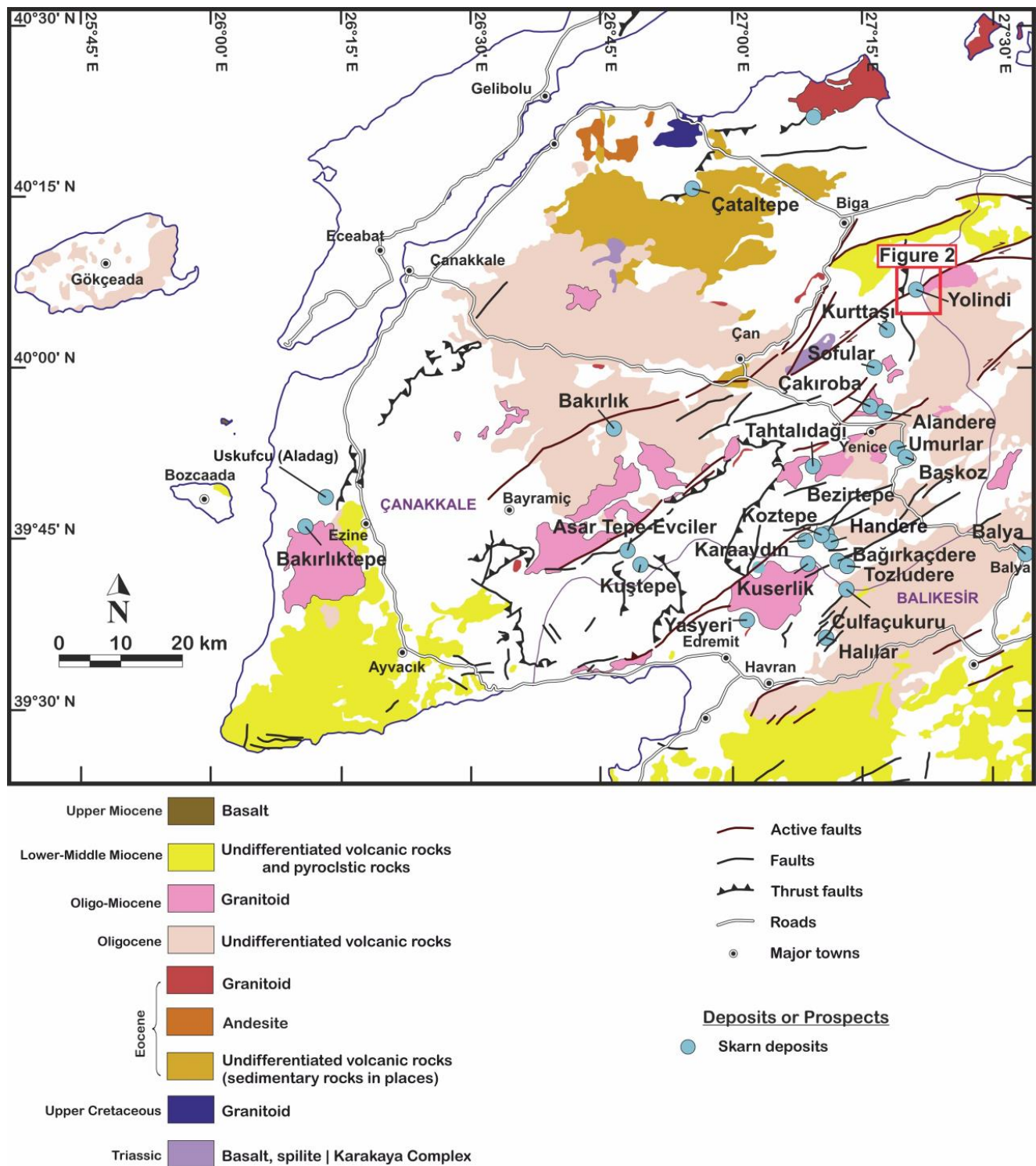


Figure 1. Distributions of the skarn deposits in the Biga Peninsula, NW Turkey, modified according to Yigit [11] and Kuşçu [5].

2. Regional Geological Background of the Biga Peninsula

Biga Peninsula (Figure 1) is a geologically diverse and complex peninsula that has been exposed to a series of tectonic events during its lengthy history. It represents the western section of the Sakarya Zone (S Pontide Domain) along the boundary between Gondwana and Laurasia [12] and consists of numerous tectonic units, representing both continental and oceanic assemblages [13]. The tectonic activity of the Biga Peninsula is primarily impacted by the motion occurring along the North Anatolian Fault Zone [14]. This fault zone divides into two primary branches, namely, the northern and southern branches, located in the eastern area of Marmara. The southern branch of the fault system has a trajectory that extends in the direction of the Biga Peninsula. This region is distinguished by a stress regime that involves strike-slip and oblique normal faulting, particularly in its center-to-northern portion. The region located in the southernmost portion of the peninsula has a stress regime that is mostly characterized by normal to oblique faulting [14]. Okay, et al. [15] identified four distinct NE–SW trending zones within the Biga and Gelibolu peninsulas. These zones, listed in order from northwest to southeast, are referred to as the Gelibolu, Ezine, Ayvacık-Karabiga, and Sakarya zones. The oldest rocks in the Biga Peninsula are metamorphic basement rocks that formed during the Precambrian to Early Paleozoic era. These basement rocks consist primarily of gneisses, schists, and marbles that underwent multiple metamorphic events under high-pressure and high-temperature conditions [16]. The peninsula also has plutonic and related volcanic rocks, ophiolites, and amphibolite to granulite facies metamorphic rocks [17,18]. Furthermore, the area has two major thrust basement rock groups: the Kazdağ metamorphic units and the Çamlıca metamorphic unit with high-pressure assemblages, as well as the Kemer metamorphics [19]. In other words, the metamorphic rocks are split into two major zones: the Ezine zone with the Çamlıca Metamorphic unit in the northwest region of the Biga Peninsula and Kazdağ Group and Karakaya Complex zone in the southeast region of the Biga Peninsula, which serve as the basement of the Rhodope and Sakarya zones, respectively [11]. Other metamorphic units occurred in the Biga Peninsula, such as the Çamlık and Yolındı Metagranodiorite, which was exposed north of the northeast region and intruded into the Kalabak Formation [20]. The main tectono-stratigraphic units in the area of the Biga Peninsula are Denizgören ophiolite and Çetmi ophiolitic mélange, which occurred in the SW and N of the Biga Peninsula, respectively [11,15]. The Biga Peninsula observed extensive tectonic processes throughout the Mesozoic era, including sedimentation, ophiolite emplacement, and the development of volcanic island arcs [12]. Sedimentation had a significant effect in creating the geology of the area throughout the Triassic era. During this period, extensive deposition of carbonate rocks such as limestones and dolomites occurred in shallow marine environments [12,21]. These carbonate rocks give evidence of Triassic marine environments on the Biga Peninsula [21]. As the Mesozoic period gave way to the Jurassic and Cretaceous periods, tectonic activity spread ophiolite complexes over the continent, as well as flysch and mélange deposits. These ophiolites and associated deposits reveal geological events such as oceanic crust formation, subduction, and accretionary processes in the area. Therefore, they are predominantly Permo-Triassic carbonates and clastic rocks of the Karakaya Complex, with Mid-Triassic to Jurassic neritic limestones of the Çetmi Ophiolitic Mélange occurring as part of several Formations, including the Bayırköy Formation, Bilecik Limestone, and Vezirhan Formation [15].

Aside from the metamorphic basement rocks, the Biga Peninsula has an extensive record of magmatic and volcanic activity dating back to the Pre-Cenozoic and Cenozoic eras (Figure 1). Granitic intrusions and volcanic rocks were emplaced on the Biga Peninsula during the Late Paleozoic era as a result of the closure of the Paleo-Tethys Ocean and the formation of the supercontinent Pangea [22]. They also took place in an extensional tectonic regime, which is characterized by the stretching and thinning of the Earth's crust. This extensional tectonic regime resulted in various unique tectonic settings such as the back-arc basin [13]; orogenic collapse [23]; slab breakoff [24]; and single-subduction zone [25]. The formation of the back-arc-type extension in the Aegean area may be attributed to the

rollback of the Hellenic subduction zone [13,26,27]. However, the orogenic collapse of the high topography thickened crust during the Eocene also contributed to the extension in the Aegean area [23]. Additionally, slab break-off, convective removal, or partial delamination of the lithosphere are the driving mechanisms responsible for syn-convergent extension and magma generation [24]. The granitic intrusions found on the Biga Peninsula are frequently accompanied with mineralization, suggesting that they might have formerly acted as a source of important metallic minerals [11]. The Late Cretaceous Şevketiye Pluton (Delaloye and Bingöl, 2000) represents the Pre-Cenozoic era in the northern part of the Biga peninsula (Figure 1). In contrast, the Cenozoic era is characterized by a variety of intrusions across the Eocene to the Oligo-Miocene, including Dikmen, Evciler, Eybek, Kestanbol, Kuşçayır, Şaroluk, and Yenice, which are mainly concentrated in the central and southern regions of the peninsula, along with the Kapıdağ and Karabiga plutons in the north [28–33]. The volcanic rocks that originated on the Biga Peninsula during this time period provide valuable insights into the ancient volcanic arcs that formed due to the subduction processes of the Neo-Tethyan oceanic lithosphere in Anatolia [34]. These volcanic rocks, together with the related mineral deposits, give vital information on the tectonic and magmatic processes that occurred in the region during the Late Paleozoic period [11]. Pre-Cenozoic volcanic rock assemblages are dominated by Triassic basic volcanic rocks such as basalts and spilites. These are found with ophiolitic mélanges, a chaotic mix of rock types, and the Karakaya Complex [11]. The Cenozoic period, on the other hand, observed the formation of Ayvacık volcanic rocks, Ezine basalt, and Taştepe basalt, all with calc-alkaline to alkaline affinities, indicating a diverse magmatic history [29,35,36]. In addition to their geological significance, the Cenozoic plutons and volcanic successions of the Biga peninsula are economically significant. The majority of the metallic mineral resources and industrial materials that have aided its economy are related to these Cenozoic formations [11,37] (Figure 1).

3. Samples and Methods

In the Yolindi area, extensive fieldwork was conducted to gain a complete understanding of the geological context. To guarantee representativeness, samples from both the primary host rocks with alteration and the altered rocks displaying mineralization were methodically collected. A total of 121 thin and 88 polished sections were prepared from the collected samples. The sections were petrographically examined using a polarizing microscope to determine the mineralogical and textural relationships within the rocks.

The 132 rock samples were geochemically analyzed at the Geochemistry Research Laboratories of Istanbul Technical University (ITU/JAL). To ensure uniformity, the samples were finely ground using a RETSCH RS-200 model milling device with a tungsten carbide milling apparatus. A BRUKER S8 TIGER model X-ray fluorescence spectrometer (XRF) with a wavelength range of 0.01–12 nm was used to evaluate the major oxides of these samples. The trace elements and rare earth elements (REE) were evaluated using an ELAN DRC-e Perkin Elmer model Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Approximately 100 mg of each powdered sample was completely digested by using BERGHOF speedwave MWS-3⁺ model microwave device for the ICP-MS analysis. The sample was initially digested in a Teflon beaker with a mixture of 6 mL of 37% HCl, 2 mL of 65% HNO₃, and 1 mL of 38%–40% HF. Afterwards, the excess of HF acid was removed with the addition of 6 mL of H₃BO₃ 5% (*w/v*) solution to vessel. The digested materials were transferred to a 50 mL volumetric flask by rinsing with pure water, and clear solutions of the samples were obtained. The same microwave technique was used to prepare a blank solution for ICP-MS analysis. At the Geochemistry Research Laboratories of Istanbul Technical University (ITU/JAL), X-ray Diffractometry (XRD) studies were carried out using a D8 ADVANCE BRUKER diffractometer to identify the minerals within the altered rock samples. Utilizing a copper-sealed tube X-ray source that emits Cu K α radiation at 1.5406 Å, this device operates with a theta: theta geometry. The operational range for X-ray energy is 3 keV to 30 keV, and it operates at 40 kV and 40 mA. The X'Pert HighScore Plus v. 3.0 software, which, additionally, assisted with the semi-quantitative evaluation of

mineral contents, was used to identify mineral phases. The Icpet version 2.3 software [38] was used for drawing REE patterns. Using the GEOISO-Windows software (version 1.0, available from the IAMG server, Porto, Portugal) [39], it was possible to assess the elemental mobility and construct an extensive overview of changes in mass balance and volume. The software allows the construction of isocon diagrams based on Grant [40] using Gresens [41] equations.

The altered and ore mineral chemistry was analyzed at the Earth Sciences Application and Research Center (YEBIM) at Ankara University using a JEOL JXA-8230 electron microprobe. The instrument operated at an accelerating voltage of 20 kV, a beam current of 20 nA, a beam size of 1–5 μm , and counting times ranging from 10–60 s. For calibration and quality assurance in the JEOL instrument, we utilized standard reference materials prepared and provided by Micro-Analysis Consultants Ltd. (MAC). The natural minerals and synthetic oxides used for calibration purposes included: albite (Na), andradite (Si, Ca), apatite (P), barite (Ba), cadmium (Cd), celestine (Sr), chromium (Cr), cobalt (Co), copper (Cu), dolomite (Ca, Mg), fluorite (F), gold (Au), halite (Cl), hematite (Fe), indium arsenate (As), lead telluride (Pb), nickel (Ni), olivine (Mg, Fe), orthoclase (Si, Al, K), palladium (Pd), platinum (Pt), pure antimony (Sb), pyrite (Si, Fe, S), rodanite (Mn), rutile (Ti), selenium (Se), silver (Ag), sphalerite (Zn), strontium fluoride (Sr), tantalum (Ta), vanadium (V), willemite (Zn), wollastonite (Si, Ca), yttrium (Y), zinc (Zn), and zircon (Zr). The Phi-Rho-Z (CITZAF; [42]) correction scheme, integrated into the JEOL JXA-8230, addressed possible matrix effects, instrumental drifts, and dead times. When the accuracy metrics were compared to standard reference materials, it was discovered that at concentrations above and below the threshold of 1 wt.%, the relative accuracy was between 1%–2% and 5%–10%, respectively.

4. Local Geology of Yolindi Area

The Yolindi area is approximately 16 km northeast of the Biga Peninsula in Çanakkale province in northwest Turkey (Figure 1). The Upper Paleozoic Kalabak Group, which comprises Torasan Formations, Yolindi metagranodiorite, and Sazak Formations, and the Triassic Karakaya Complex, constitute the area. The Early Miocene Hallaçlar volcanics and Early Miocene Şaroluk granitoids intruded into these rocks (Figure 2). Below is a quick summary of these significant lithostratigraphic units.

The Kalabak Group is the basement of the Sakarya Zone, which is a distinct tectonic unit. It is mostly made up of rocks that have been subjected to low-grade metamorphism [43]. It was classified into two formations, with the Torasan Formation being the lowermost unit and the Sazak Formation representing the uppermost unit. The Torasan Formation is composed of epiclastic rocks that have undergone low-grade metamorphism. On the other hand, the Sazak Formation includes pyroclastic lithologies. The presence of metagranitic rocks that overlap, notably with the Torasan Formation, is an uncommon aspect of the Kalabak Group, known as the Yolindi Metagranodiorite (Figure 2). The Upper Paleozoic Torasan Formation (Pzt) is known as Torasan metamorphic rocks by Okay, et al. [15]. It is located in the western part of the study area, around Yolindi village and Bıçkı and Baltaoluk hill (Figure 2). It is primarily composed of phyllites and muscovite-, biotite-, talc-, tremolite-, and chlorite-schists and their tuffs, with hornfels, metasandstone, and metasiltstone metamorphosed under low-to medium-grade metamorphic conditions. The phyllite and schists of the Torasan Formation, as well as its tuffs, are generally gray and greenish yellow in color, having foliation (Figure 3a). Within the phyllites, serpentinized peridotites (Pzts) (Figure 3b), talc-antigorite schists, and marble members (Pztm) (Figure 3c) have scattered as blocks and lenses (Figure 2). A well-developed foliation of muscovite, biotite, and quartz with opaque minerals characterizes the fine-grained texture of phyllite (Figure 3d). Biotite schists are distinguished by their schistose texture and mostly include biotite and quartz with a few opaque minerals. (Figure 3e). Actinolite hornfels are a contact metamorphic rock that include actinolite and quartz with clinozoisite, clinopyroxene, and opaque minerals (Figure 3f). The serpentinites in these lenses, which have undergone low-grade metamorphism, are made up of antigorite with chlorite, clinopyroxene remnants,

and less common opaque minerals (Figure 3g). Marble and recrystallized limestone, on the other hand, are fine-grained and compact boulders with a white-gray tint, forming lenses 1–40 m thick and spanning thicknesses of 3–10 m (Figure 3c), composed mainly of calcite (Figure 3h). Yolindi metagranitoids (Pzy), on the other hand, are distinguished by brownish, medium-grained, significantly altered biotite gneiss, granitic porphyry, and metagranodiorite with directional textures and rare intrusions of dacitic and aplitic dykes. Their U-Pb zircon SHRIMP and LA-ICP-MS dating gave Early Middle Devonian ages [8]. As well, their considerable outcrops may be seen to the north of the study area, towards Yolindi village (Figures 2 and 3i). They are usually tectonically bounded on the western side by the Torasan Formation and unconformably covered on the eastern side by the Karakay Formation, extending in a NE-SW direction [15,44,45] (Figure 2). Biotite gneiss is characterized by the presence of mineral bands that are often differentiated into distinct light and dark bands. Biotite is a significant constituent in this rock with quartz, sericitized plagioclase, and some opaque minerals (Figure 3j). However, altered granodiorite porphyry comprises phenocrysts of sericitized plagioclase embedded in a groundmass of fine-grained kaolinitized feldspar, quartz, and opaque minerals (Figure 3k). Sericitized plagioclase, quartz, biotite, and opaque minerals make up metagranodiorite (Figure 3l). The Sazak Formation, which overlaps the Torasan Formation in the north of the study area, has a steady increase in tuff levels. It is made up of greenish fine-grained, well-foliated basic metatuffs, metavolcanites, tremolite-actinolite schist, and marble [15].

The Triassic Karakaya Complex (TrKK) covers the central and westernmost portions of the study area, which are found near the villages of Inova and Tahtali (Figure 2). In terms of structural categorization, Okay and Goncoglu [46] divided this complex into lower metamorphic rocks (of low grade) and upper metamorphic rocks (of high grade). The Yolindi area has the lower Karakaya Complex, which is characterized by a succession of metasandstone with alternating layers of fine-grained phyllite, metavolcanics, and serpentinites (Figure 4a). Metasandstone primarily consists of sand-sized particles of quartz with sericite, muscovite, K-feldspar, and iron oxides (Figure 4b). A very fine foliation of biotite, k-feldspar, and sericite is arranged with quartz and muscovite in phyllite (Figure 4c).

The Early Miocene Şaroluk granitoid (MŞ) occurred as a pluton, which extends in an east–west direction and spans an area of 20 km², exhibiting an elliptical surface exposure (Figure 2). Its U-Pb zircon dating varied from 22.18 ± 0.40 to 21.51 ± 0.37 Ma, displaying that this particular pluton magmatism formed during the Early Miocene [6]. At the western boundary of this pluton, in conjunction with the Torasan Formation and the pluton, a hornfels zone has formed (Figure 3f). Fresh, unaltered, large-block-sized rocks could be observed in the eastern part of the Şaroluk Pluton, whereas the western region has undergone significant alteration. The rocks predominantly exhibit black to white colors, except for zones with significant alteration, which are creamy. The joint sets on the pluton are oriented N80° W/50° SE and run parallel to each other (Figure 4d). Quartz monzonite dominates the Şaroluk pluton, with minor quantities of granodiorite and monzonite being observed. A completely crystalline, porphyritic to granular texture including plagioclase (34%–41%), K-feldspar (20%–27%), quartz (13%–19%), biotite, and tremolite make up the majority of these rocks, with sericite, chlorite, epidote, and opaque minerals (Figure 4e). Plagioclase (50%–70%), quartz (20%–30%), and microperthite (5%–15%) are the main constituents of granodiorite, along with hornblende, biotite, trace amounts of pyroxene, and other opaque minerals (Figure 4f). The pluton also contains gray microgranular patches of microgranophyre that have sizes up to 10 cm (Figure 4g). The microgranophyre has a granophyric texture and is significantly finer-grained, including mostly quartz and microperthite with biotite and opaque minerals (Figure 4h).

The Hallaçlar Formation (Toh) is widely exposed in the southwest of the study area, close to the Beyoluk village and around Bayındırlık Hill, Koca Hill, and Deniz Hill (Figure 2). It was dated at 23.6 Ma by Krushensky [45], whereas 26.5 ± 1.1 Ma was determined by Dönmez, et al. [47]. Karacik, et al. [48] estimated the age of this formation to be 22.6 ± 0.8 Ma. As a result, the volcanic activity that started in the Late Oligocene continued

throughout the Early Miocene. The exposed parts of the Hallaçlar Formation are primarily yellowish, whitish, and brownish (Figure 4i), while the altered sections are notably gray and pale yellow (Figure 4j). It includes porphyritic andesite, rhyodacite, felsic tuffs, tuffaceous siltstone, and pyroclastics. These rocks have undergone kaolinization, hematization, and limonitization. Porphyritic andesite is mostly formed of hornblende, biotite, and plagioclase phenocrysts embedded in fine-grain microcrystalline plagioclase laths, biotite, hornblende, quartz, and opaque minerals (Figure 4k). Felsic metatuffs are metamorphosed volcanic tuffs that previously had a felsic composition and are rich in light-colored minerals such as quartz and feldspars with sericite and kaolinite (Figure 4l).

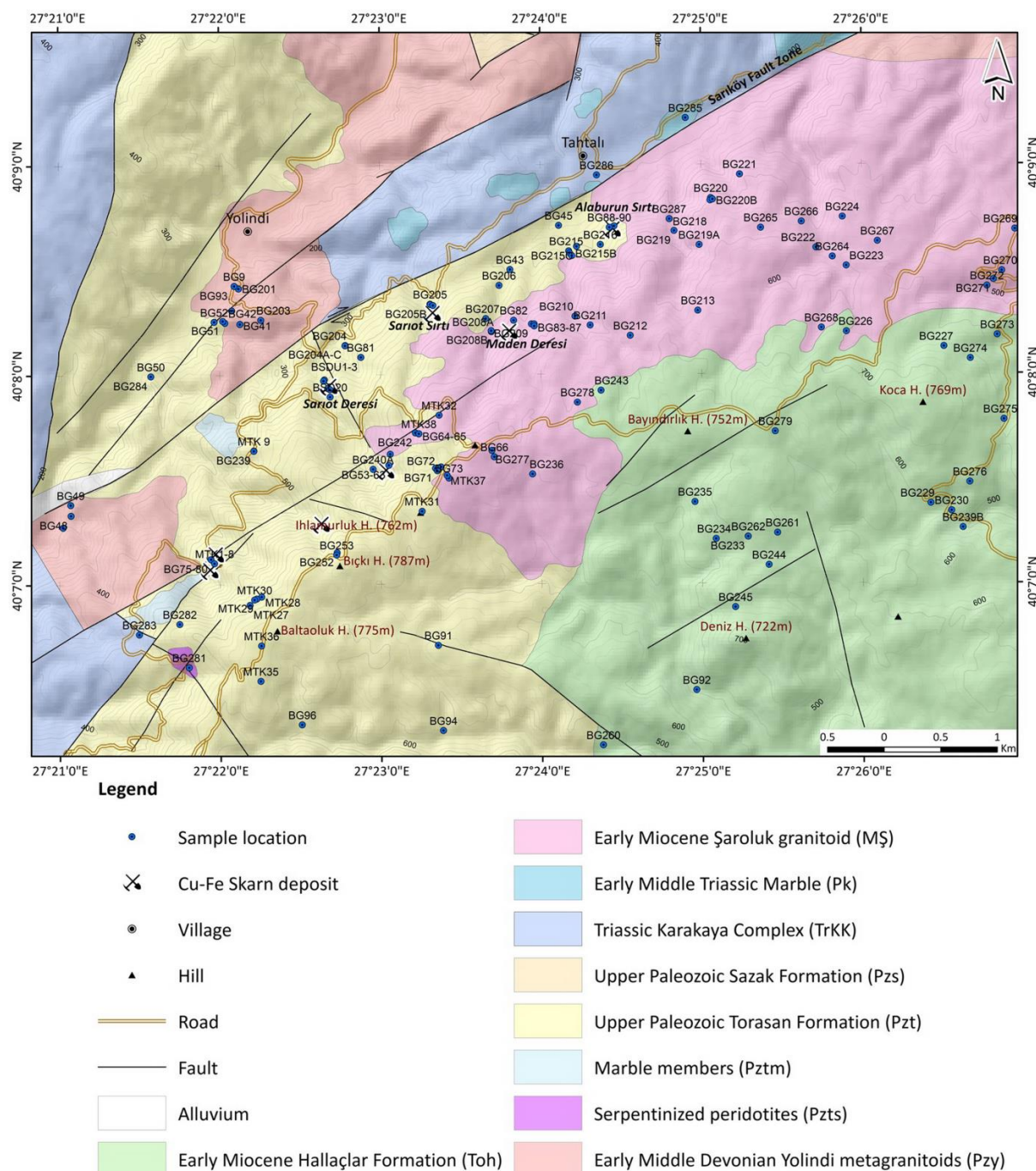


Figure 2. Geologic map of the Yolindi area modified according to Duru, et al. [10], Aysal [9], and Aysal, et al. [8].

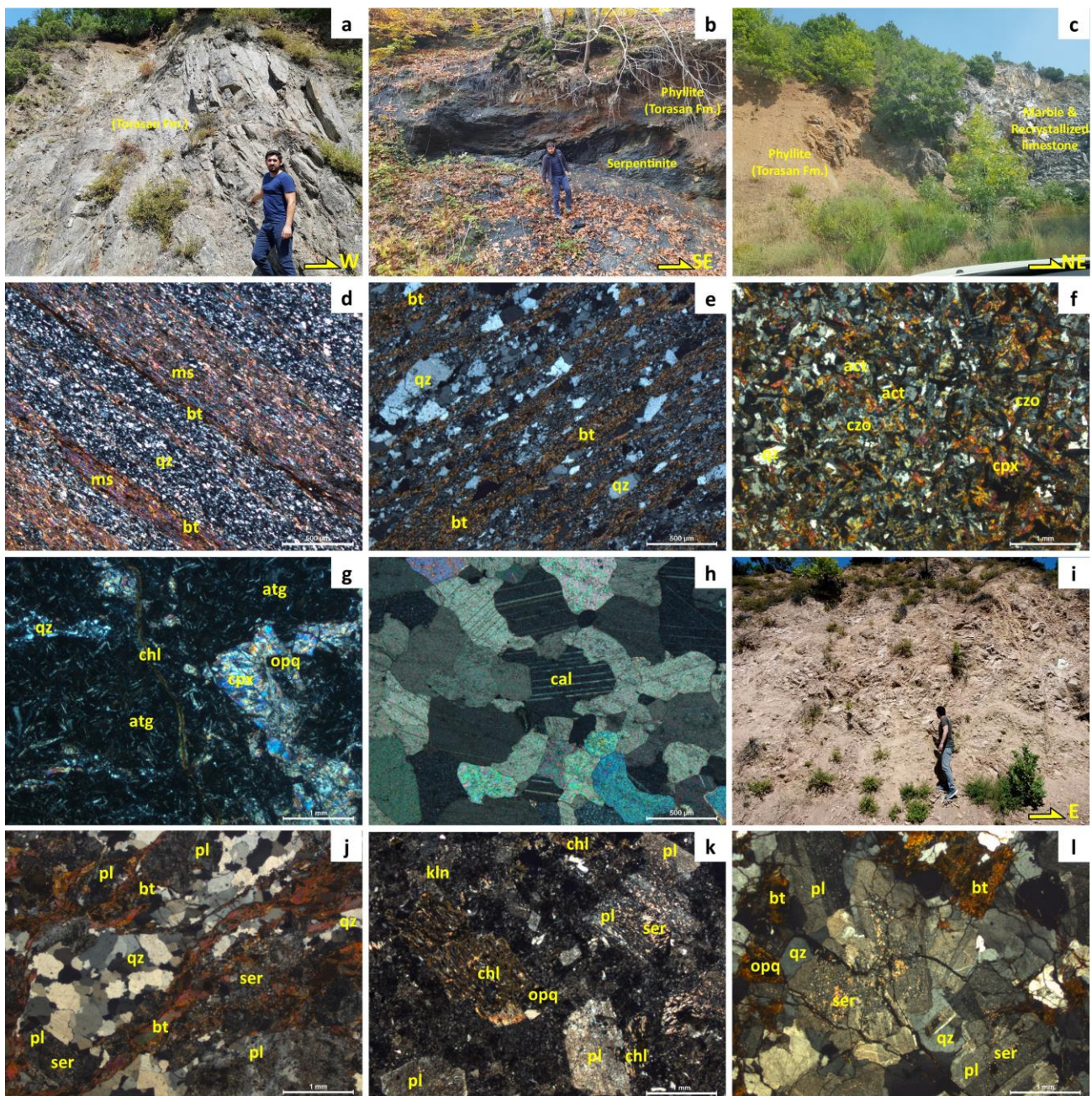


Figure 3. (a) Foliation of the phyllite of the Torasan Formation. (b) Serpentinized peridotites associated with Torasan Formation. (c) Marble and recrystallized limestone in association with Torasan Formation. (d) Phyllite has well-developed foliation of muscovite, biotite, and quartz with opaque minerals. (e) Biotite and quartz with a few opaque minerals in biotite schists. (f) Actinolite and quartz with clinozoisite, clinopyroxene, and opaque minerals in actinolite hornfels. (g) Serpentinites consist of antigorite with chlorite, clinopyroxene remnants, and less common opaque minerals. (h) Calcite is the main constituent of marble. (i) General view of the Yolindi metagranitoids. (j) Biotite gneiss having biotite with quartz, sericitized plagioclase and some opaque minerals. (k) Phenocrysts of sericitized plagioclase in a groundmass of fine-grained kaolinitized feldspar, quartz, and opaque minerals in altered granodiorite porphyry. (l) Metagranodiorite contains sericitized plagioclase, quartz, biotite, and opaque minerals. Abbreviations: actinolite (act), antigorite (atg), biotite (bt), calcite (cal), chlorite (chl), clinopyroxene (cpx), clinozoisite (czo), kaolinite (kln), muscovite (ms), opaque mineral (opq), plagioclase (pl), quartz (qz), sericite (ser).

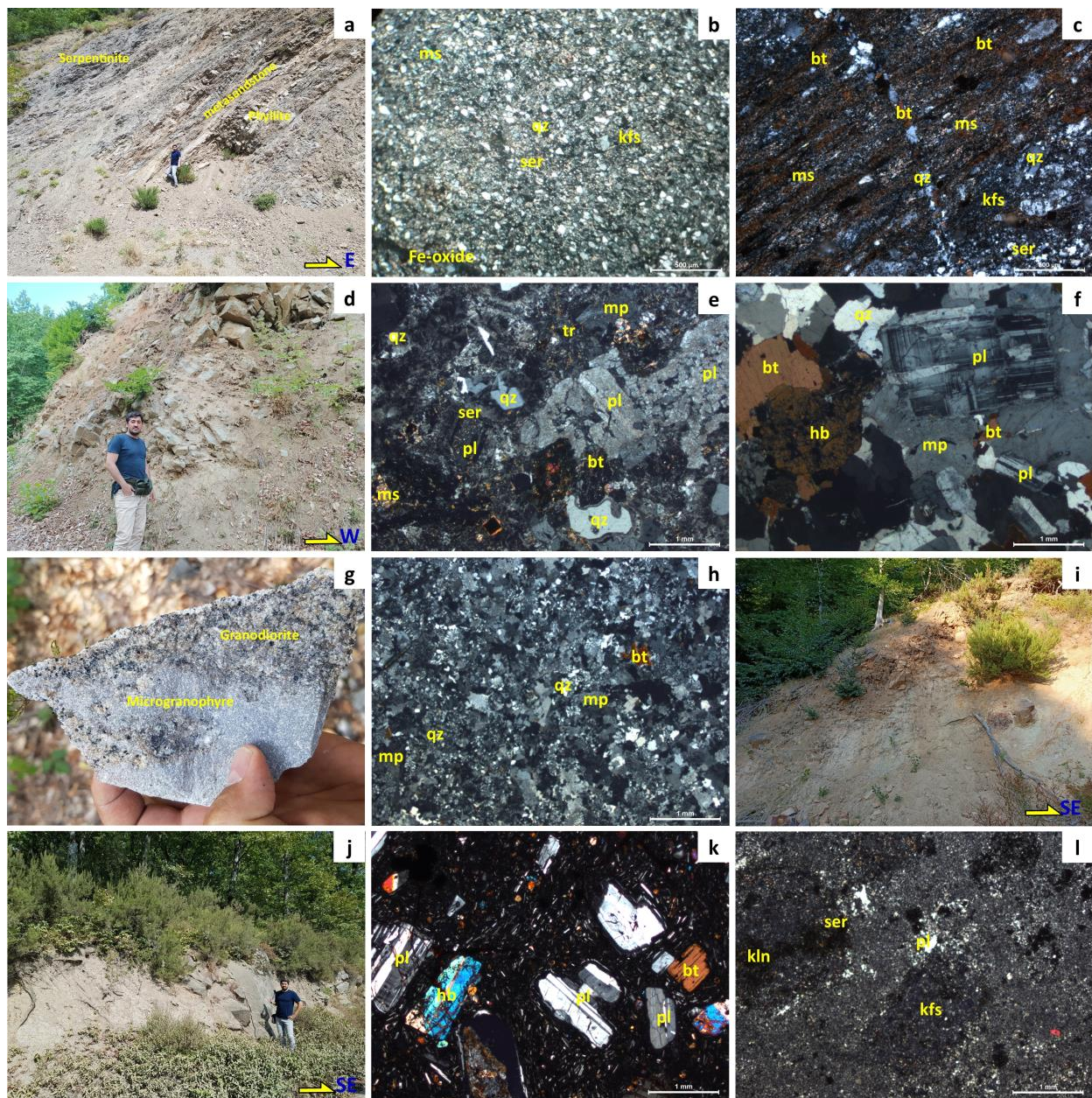


Figure 4. (a) Succession of metasandstone with alternating layers of fine-grained phyllite and serpentinites within the Karakaya Complex. (b) Quartz with sericite, muscovite, K-feldspar, and iron oxides in the metasandstone. (c) Phyllite consists of biotite, k-feldspar, and sericite, with quartz and muscovite. (d) Joint sets on the Şaroluk granitoid pluton are oriented N80° W/50° SE and run parallel to each other. (e) Plagioclase, K-feldspar, quartz, biotite, and tremolite make up most of the quartz monzonite. (f) Granodiorite, composed of plagioclase, quartz, and microperthite with hornblende, biotite, and other opaque minerals. (g) Microgranular patches of microgranophyre in the grandiorite of the Şaroluk pluton. (h) Fine-grained granophyric texture has quartz and microperthite, with biotite and opaque minerals in the microgranophyre. (i) The exposed parts of the Hallaçlar Formation have yellowish, whitish, and brownish exposure. (j) Gray and pale yellow of the felsic metatuffs. (k) Hornblende, biotite, and plagioclase phenocrysts embedded in fine-grain microcrystalline plagioclase laths, biotite, hornblende, quartz, and opaque minerals in the porphyritic andesite. (l) Quartz and feldspars with sericite and kaolinite in the felsic metatuffs. Abbreviations: biotite (bt), hornblende (hb), K-feldspar (kfs), kaolinite (kln), microperthite (mp), muscovite (ms), plagioclase (pl), quartz (qz), sericite (ser).

5. Results

5.1. Hydrothermal Alterations and Mineralization of the Yolindi Skarn Deposit

The Cu-Fe($\pm$ Zn $\pm$ Pb) skarn deposit in the Yolindi area is a part of the broad magmatic-hydrothermal system in the Biga peninsula (NW Turkey), which was formed due to the intrusion of the Early Miocene Şaroluk granitoid (having mainly quartz monzonite with less granodiorite) into the Upper Paleozoic Torasan Formation (having phyllites and muscovite-, biotite-, talc-, tremolite-, and chlorite-schists and their tuffs, with hornfels, metasandstone, and metasiltstone) within a zone of the calc-silicate and hornfels zones. Generally, Cu mineralization is frequently associated with Fe-skarns. Cu is typically discovered in irregular pockets with magnetite ore bodies. Trace quantities of Au mineralization can be found in a few Fe-skarns with favorable Cu mineralization. In the study area, the zonal alteration patterns can run concentrically or perpendicular to the contact between the Şaroluk granitoid intrusion and the Torasan Formation and carbonate-rich rock/limestone. These zones, which are often classified as endoskarns and exoskarns depending on their proximity to the intrusion, as well as three subzones based on their proximity to the intrusive body: proximal, intermediate, and distal zones, are often expressed by mineral assemblages (Figure 5).

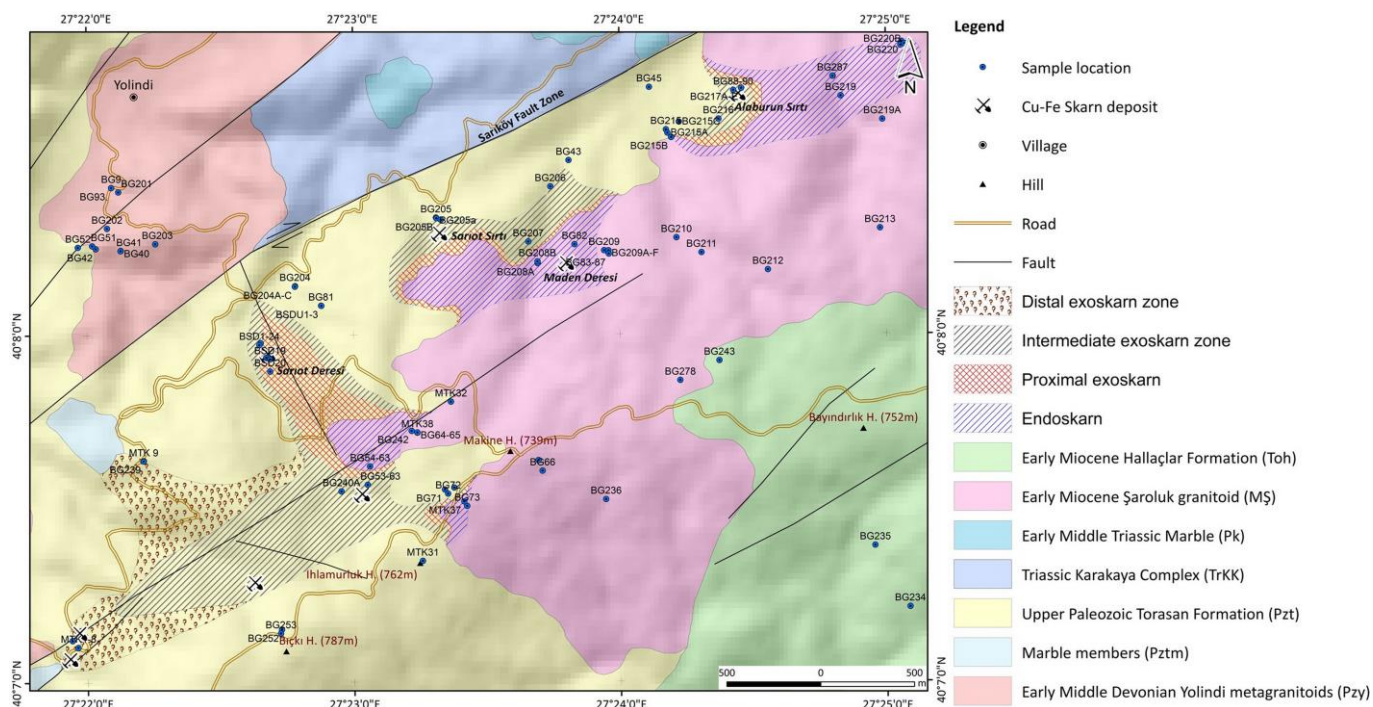


Figure 5. Zonation map of the Yolindi Cu-Fe Skarn deposit showing the different skarn zones: endoskarn and proximal, intermediate, and distal exoskarn zones.

The Torasan Formation granitoid contacts, in particular, are where the Şaroluk quartz monzonite has bleached from grey to whitish, brownish, and greenish, making the endoskarns readily apparent in the field (Figures 5 and 6a). The endoskarn was formed within the Şaroluk intrusive body itself, typically in its outer regions, and located around the Maden Deresi and İmameğreği Sırtı areas (Figures 2 and 5). Mesoscopically, fresh granitoid patches and the occurrences of skarnized granitoids (which include andradite) may both be used to detect the formation of garnet, followed by epidote and sericite during metasomatism. Magnetite and pyrite are present in significant amounts in this zone (Figure 6). In the Maden Deresi area, as a particular change from the low-altered magnetite-bearing granodiorite to the magnetite-bearing endoskarn, the degree of alteration increases outward to the contact region (Figure 6a). The magnetite-bearing granodiorites have mainly quartz, plagioclase, microperthite, biotite, hornblende, pyroxene, and sphene with mag-

netite (Figures 6a–d and 7a and Appendix A), whereas the magnetite-bearing endoskarn has andradite and epidote with magnetite and goethite minerals, in which andradite is the early product (Figures 6a,e–g and 7b and Appendix B). On the other hand, the İmameğreği Sirtı area is characterized by magnetite- and pyrite-bearing granodiorite, having quartz, plagioclase, microperthite, biotite, diopside, actinolite, and sphene with magnetite, pyrite, and hematite (Figures 6h–k and 7a).

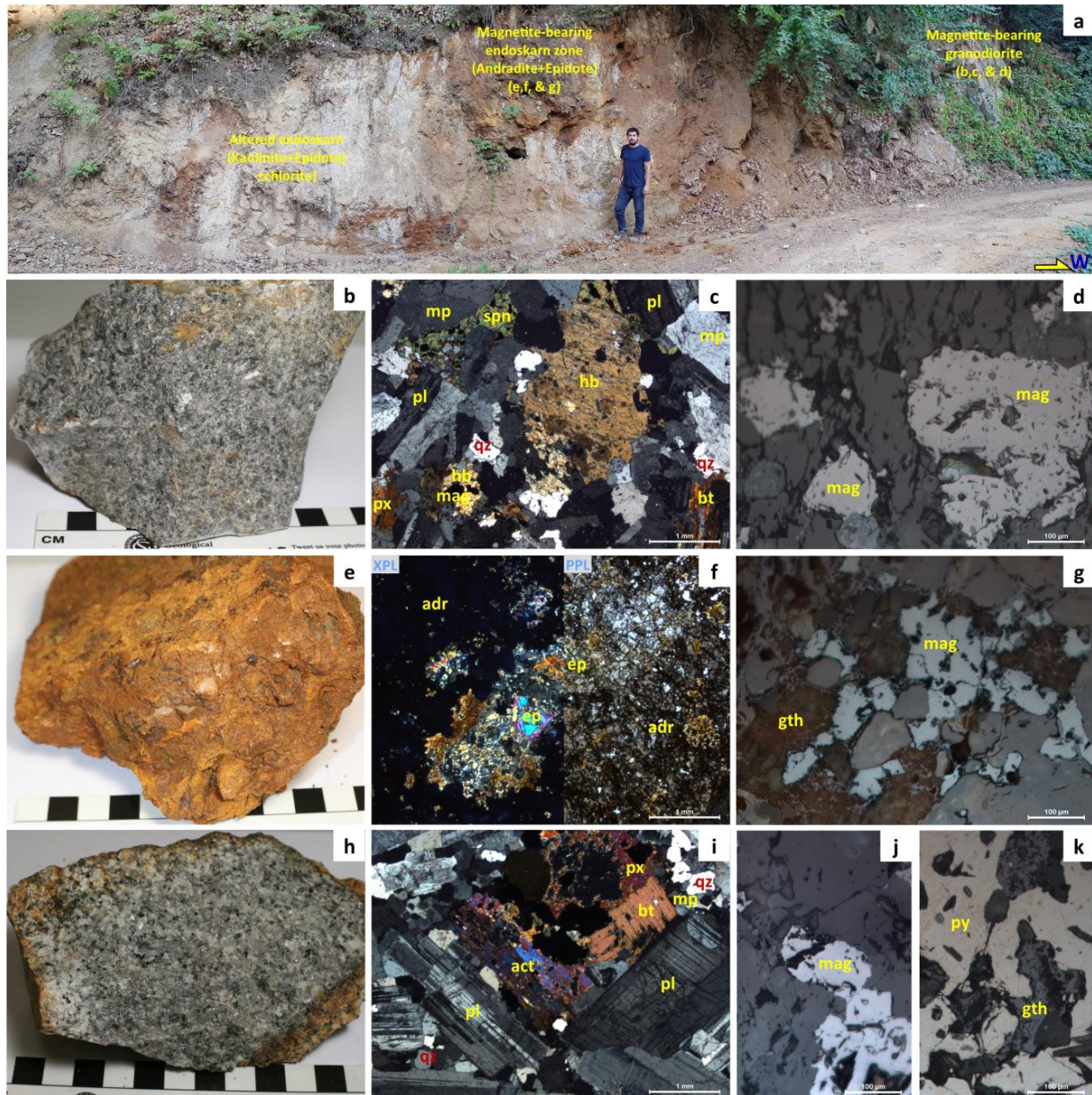


Figure 6. General features of the endoskarn zone within the Şaroluk intrusive body (a) Changes from the low-altered magnetite-bearing granodiorite to the magnetite-bearing endoskarn in the Maden Deresi area. (b,c) Magnetite-bearing granodiorites. (d) Magnetite occurred in the granodiorite in the Maden Deresi area. (e–g) Magnetite-bearing endoskarns containing andradite and epidote, as well as magnetite and goethite minerals. (h–k) Magnetite- and pyrite-bearing granodiorite having quartz, plagioclase, microperthite, biotite, diopside, actinolite, and sphene with magnetite, pyrite, and hematite. Abbreviations: actinolite (act), andradite (adr), biotite (bt), epidote (ep), goethite (gth), hornblende (hb), magnetite (mag), microperthite (mp), plagioclase (pl), pyroxene (px), pyrite (py), quartz (qz), sphene (spn).

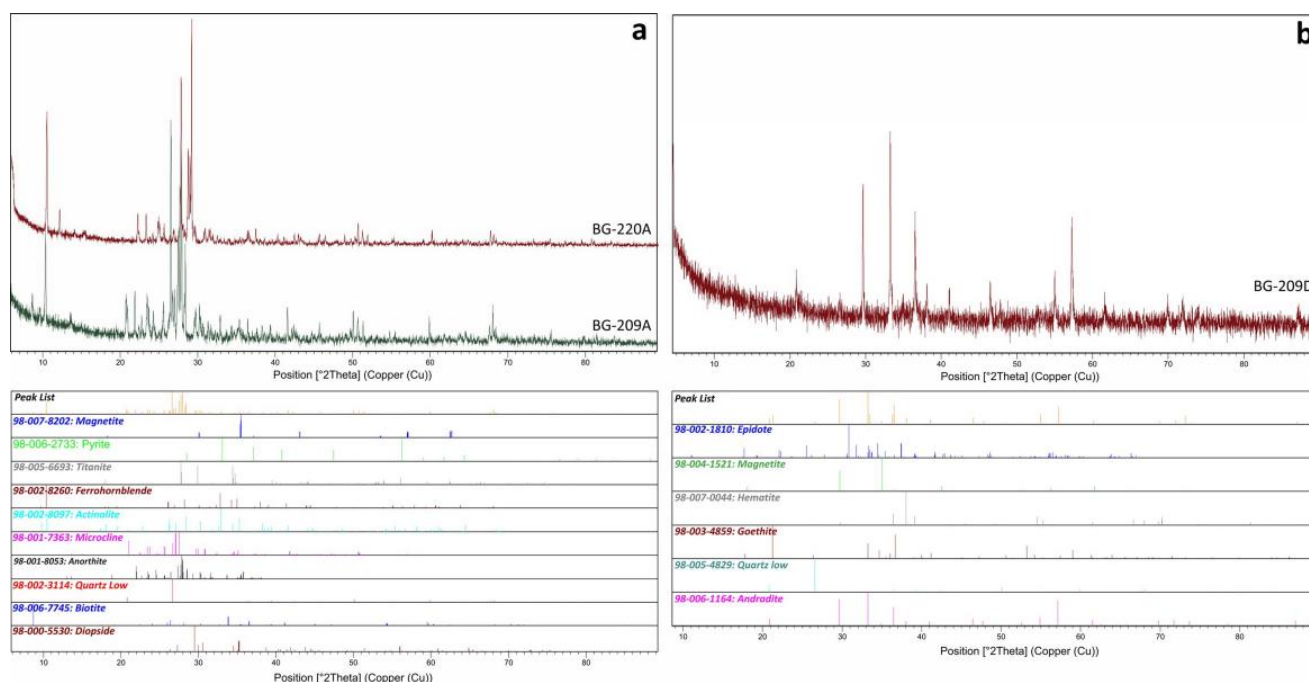


Figure 7. XRD patterns of some selected altered samples collected from the different skarn zones: (a) magnetite-bearing granodiorites. (b) magnetite-bearing endoskarn.

Exoskarns, which occur surrounding the Şaroluk granitoid body in the country Torasan formation (Figure 5), frequently contain garnet, pyroxene, epidote, scapolite, wollastonite, and ore minerals including magnetite, pyrite, chalcopyrite, bornite, hematite, and maybe sphalerite and galena (Figures 8–10). These mineral assemblages have a particular zoning pattern that corresponds to changes in fluid composition and temperature. Depending on their distance from the intrusive body, Meinert [4] grouped these zonal patterns into three subzones: proximal, intermediate, and distal zones.

Prograde and retrograde subzones make up the *proximal exoskarn zone*. In the SE of the Sariat Deresi area, the proximal prograde exoskarn zone (garnet- and magnetite-rich), which is the earliest stage of the skarn system closest to the intrusive body, is frequently distinguished by high-temperature mineralogy, which results from the interaction of fluids from the intrusive body with the nearby country rocks (Figures 2 and 5). It is distinguished by having zones of dark garnet (zoned andradite) and magnetite zones with subordinate hematite (martitization) throughout the actinolite hornfels rocks of the Torasan Formation (Figures 8a–f and 9a and Appendix C). The primary constituent of the actinolite hornfels is actinolite, which displays hornfelsic textures with quartz and opaque minerals such as magnetite and a trace amount of hematite (Figure 8e–f). On the other hand, the retrograde stage entails the alteration of prograde skarn minerals at lower temperatures and pressures while still being affected by metasomatic fluids. As a result, high-temperature prograde minerals can disintegrate, and new mineral assemblages can develop. Therefore, in the northwest of the Sariat Deresi area (Figure 5), the proximal retrograde exoskarn zone (epidote-, actinolite-, and clinopyroxene-rich) reflects a cooler and less pressurized phase of skarn formation close to the associated intrusive body. It is characterized by a greenish color (Figure 8g–h) and retrograde minerals such as epidote and actinolite with clinopyroxene relics and andradite-grossular intergrowth cut by quartz-carbonate veins (Figures 8h–j and 9b and Appendix D). A significant occurrence of ore minerals includes pyrite, chalcopyrite, bornite, hematite, and fewer magnetite (Figure 8k,l).

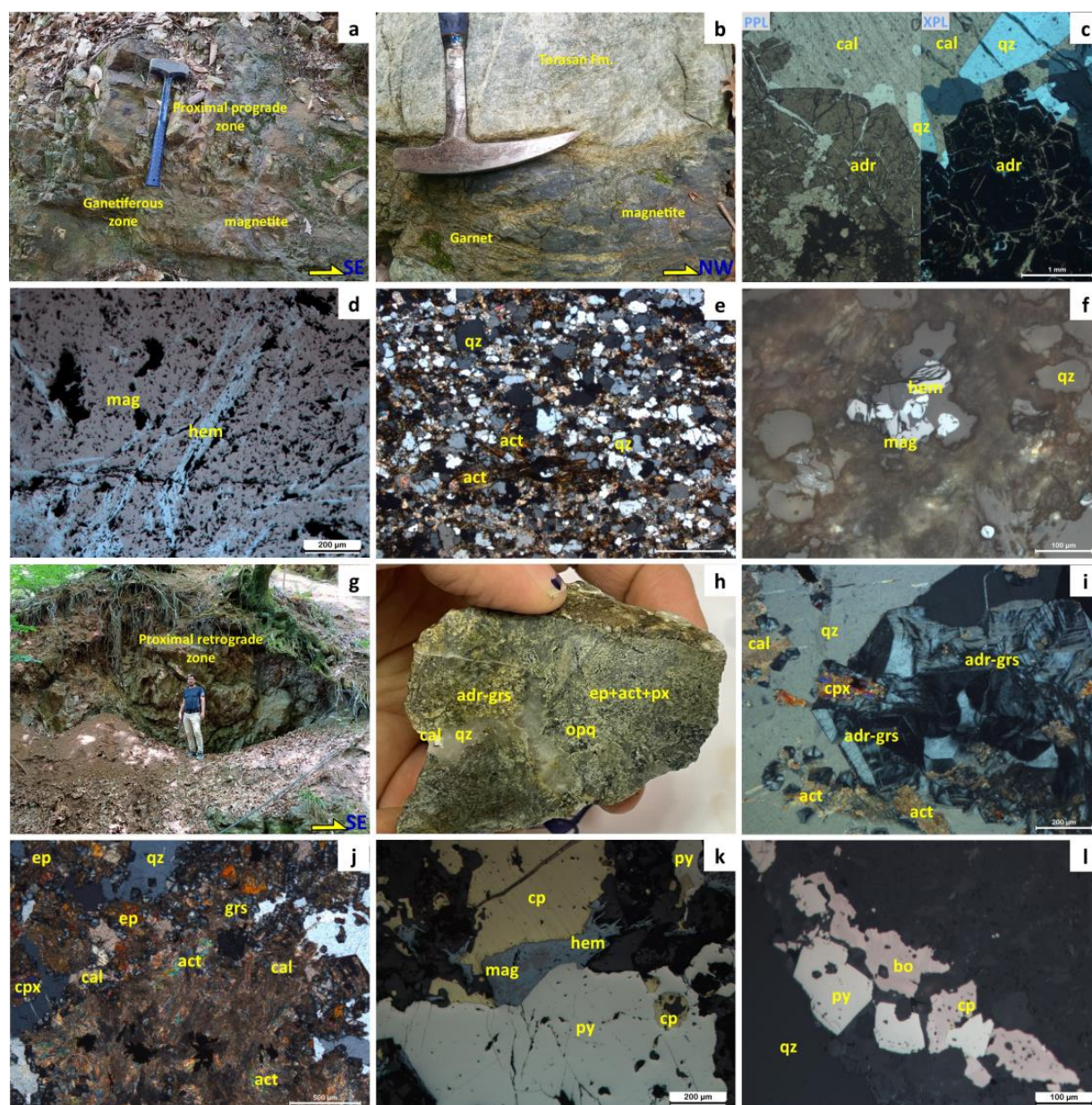


Figure 8. Characteristics of the prograde and retrograde proximal zones. (a,b) Garnet- and magnetite-bearing prograde proximal zones within the hornfels of the Torasan Formation. (c) Andradite, calcite, and quartz in the proximal zone. (d) Martitization of magnetite into hematite. (e) Actinolite and quartz in actinolite hornfels. (f) Magnetite and hematite in actinolite hornfels. (g,h) The greenish color of the retrograde proximal zone, which is cut by a quartz carbonate vein. (i,j) andradite–grossular intergrowth, actinolite, epidote, clinopyroxene relics, and quartz in the retrograde proximal zone. (k,l) Pyrite, chalcopyrite, bornite, hematite, and fewer magnetites in the retrograde proximal zone. Abbreviations: actinolite (act), andradite (adr), bornite (bo), calcite (cal), chalcopyrite (cp), clinopyroxene (cpx), epidote (ep), grossular (grs), hematite (hem), magnetite (mag), pyroxene (px), pyrite (py), quartz (qz).

In the Torasan Formation, the *intermediate exoskarn zone* (garnet-, pyroxene-, calcite-, and scapolite-rich) formed in the Sariat Sirtı, Ihlamurluk Tepe, and Alaburun Sirtı areas (Figure 5). Moving further away from the heat source at the Şaroluk granitoid pluton, the conditions are a little less extreme, and the skarn mineralogy changes. This zone has its own distinct characteristics that reflect the gradual transition from the high-temperature, magma-influenced proximal zone to the cooler, more distal retrograde zone, giving a greenish

and brownish appearance because of alteration (Figure 10a). The mineral composition of this zone is frequently diversified, including garnet (andradite–grossular), pyroxenes, and calcite with opaque minerals (Figure 10b–d). Minerals such as epidote, scapolite, and chlorite are formed as well (Figures 10b–d and 11a and Appendix E), indicating a transition from high-temperature minerals to lower-temperature and retrograde ones due to variations in temperature and fluid composition during skarn formation. Chalcopyrite, pyrite, and specular hematite represent the ore minerals formed in this zone (Figure 10e,f).

Furthermore, the *distal exoskarn zone* (epidote-, chlorite-, calcite-, and sericite-rich) within the Torasan Formation occurred in the Bıçkı Tepe region, indicating the farthest zones from the Şaroluk granitoid pluton (Figures 2 and 5) and generally having lower temperature and pressure conditions than the proximal and intermediate zones, and thus, having distinct mineral assemblages (e.g., lowest temperature minerals: epidote, chlorite, calcite, dolomite, and sericite with galena, sphalerite, and fewer chalcopyrite) (Figures 10g–l and 11b). Cerussite, covellite, and malachite are the alteration products of galena, sphalerite, and chalcopyrite, respectively (Figures 10j–l and 11b and Appendix F). As a result, this zone is typically a retrograde alteration zone in which early formed skarn minerals (including garnet and pyroxene) are overprinted and replaced by minerals generated at lower temperatures and pressures.

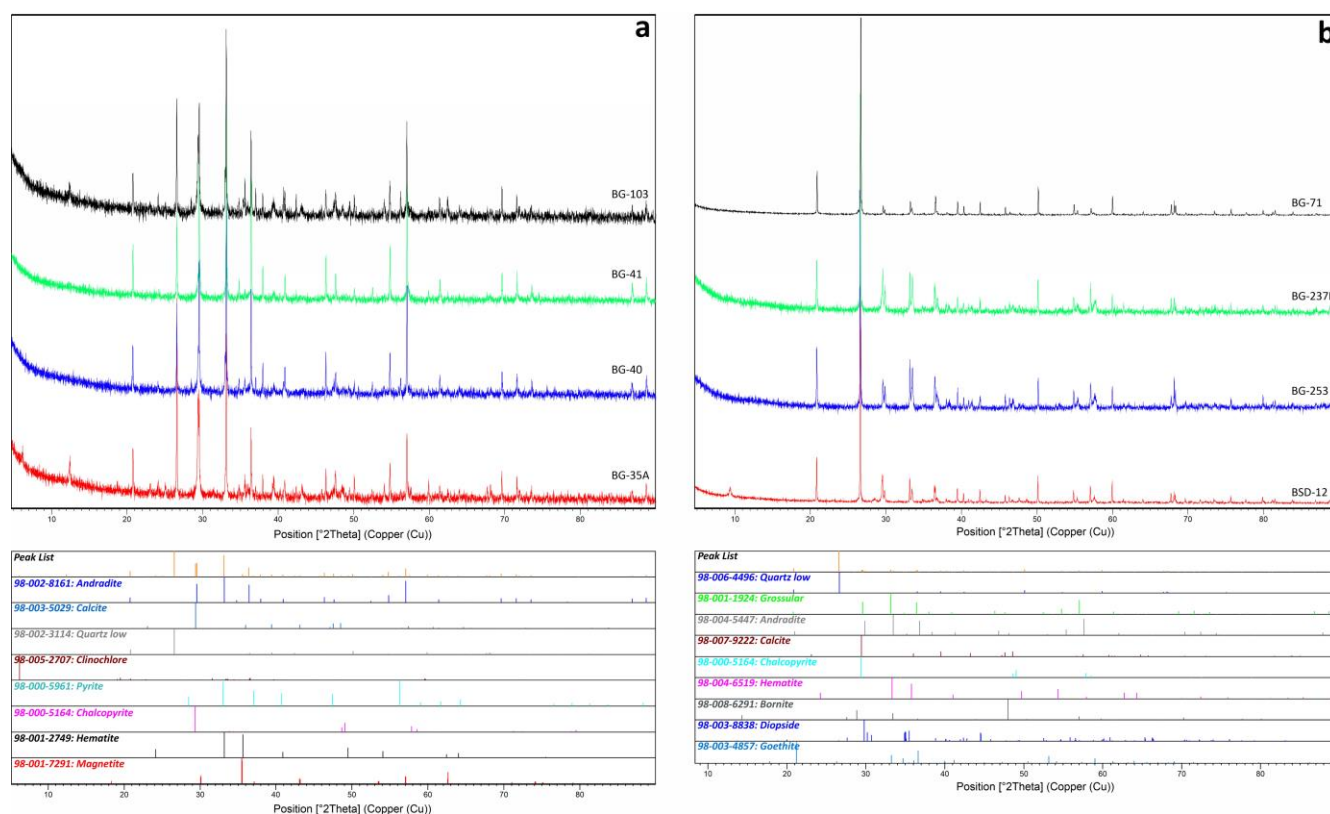


Figure 9. XRD patterns of some selected altered samples collected from the different skarn zones: (a) Prograde proximal zones. (b) Retrograde proximal zones.

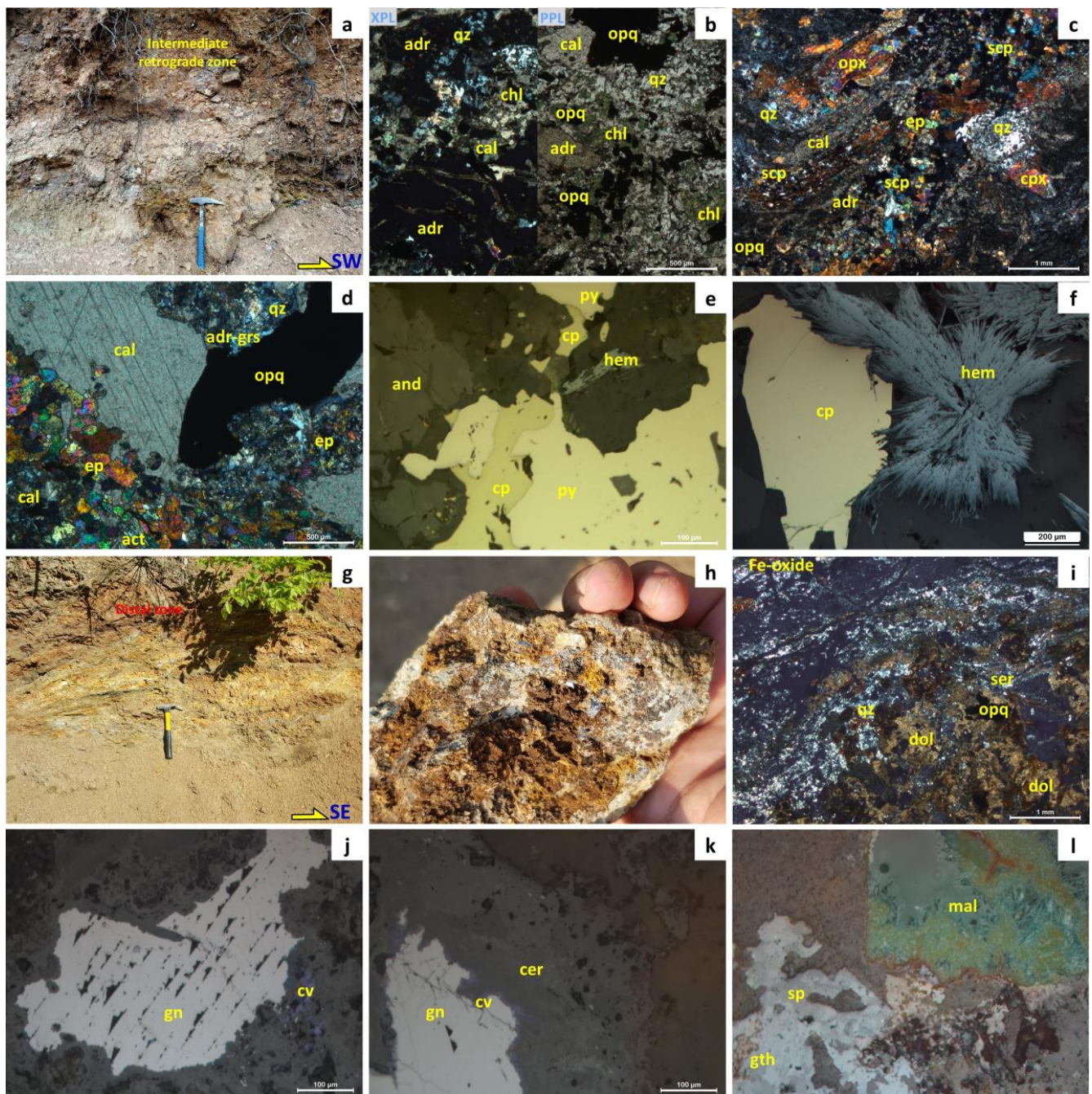


Figure 10. (a) Green and brown color alteration of the intermediate exoskarn zone. (b–d) Garnet (andradite–grossular), pyroxenes, and calcite with opaque minerals in the intermediate exoskarn zone. (e,f) Chalcopyrite associated with pyrite and specular hematite in the intermediate exoskarn zone. (g–i) Sericite and carbonate alteration of the distal exoskarn zone. (j–l) Cerussite, covellite, and malachite are the alteration products of galena, sphalerite, and chalcopyrite, respectively. Abbreviations: actinolite (act), andradite (adr), calcite (cal), cerussite (cer), chlorite (chl), chalcopyrite (cp), clinopyroxene (cpx), dolomite (dol), epidote (ep), galena (gn), grossular (grs), goethite (gth), hematite (hem), malachite (mal), opaque mineral (opq), orthopyroxene (opx), pyrite (py), quartz (qz), scapolite (scp), sericite (ser), sphalerite (sp).

5.2. Whole Rock Geochemistry

5.2.1. Geochemistry of the Yolindi Metagranodiorite and Şaroluk Granitoid Rocks

Table 1 provides the whole rock major, trace, and rare earth element (REE) data for the Yolindi metagranodiorites and Şaroluk granitoids. The LOI of all samples is less than 2.13 wt.%, with an average of 1.15 wt.%. The SiO₂ content of the Yolindi metagranodiorite rocks is greater (65.68–72.98 wt.%) than that of the Şaroluk granitoid rocks, which ranges from 56.0 to 63.17 wt.% (Table 1). Yolindi metagranodiorites contain high alkalis (K₂O + Na₂O = 6.40–7.84 wt.%), high Al₂O₃ (12.42–15.71 wt.%), and low MgO (0.65–1.15 wt.%) content. The Şaroluk granitoid rocks exhibit more alkalis (K₂O + Na₂O = 6.90–8.12 wt.%), are higher in Al₂O₃ (15.34–17.48 wt.%) and moderate MgO (1.97–3.59 wt.%) than the Yolindi metagranodiorites (Table 1). On the TAS classification diagram of Middlemost [49] (Figure 12a), the Yolindi metagranodiorites and the Şaroluk granitoids mostly fall into the granite and granodiorite and quartz monzonite and monzonite fields, respectively. Due to the enrichments of total alkalis (Na₂O + K₂O) in the analyzed granitoid rocks, they have calc-alkaline affinities [50,51] that primarily follow the trends of compressional suites (such as subduction-related granites) (Figure 12b), with intermediate unimodal frequency patterns of differentiation index and normative plagioclase [52]. According to the alumina saturation index (ASI) value (molar Al₂O₃/CaO + Na₂O + K₂O) of Shand [53], the majority of Yolindi metagranodiorites have A/CNK values greater than 1.1 and are categorized as S-type granitic suites, whereas the Şaroluk granitoids have A/CNK values below 1.1 and are classified as I-type granitic suites (Figure 12c). The Fe₂O₃ + TiO₂-FeO + MnO-MgO diagram [54] identifies the Yolindi metagranodiorites clearly as granitoids in the magnetite series (Figure 12d), and it also classifies them primarily into S-type granites and volcanic-arc granites with post-collision granites (Figure 12e,f). While the Şaroluk granitoids are clearly defined as belonging to the magnetite series (Figure 12d), I-type (Figure 12e), and volcanic-arc granite (VAG) with post-collision granite (PCG) (Figure 12f).

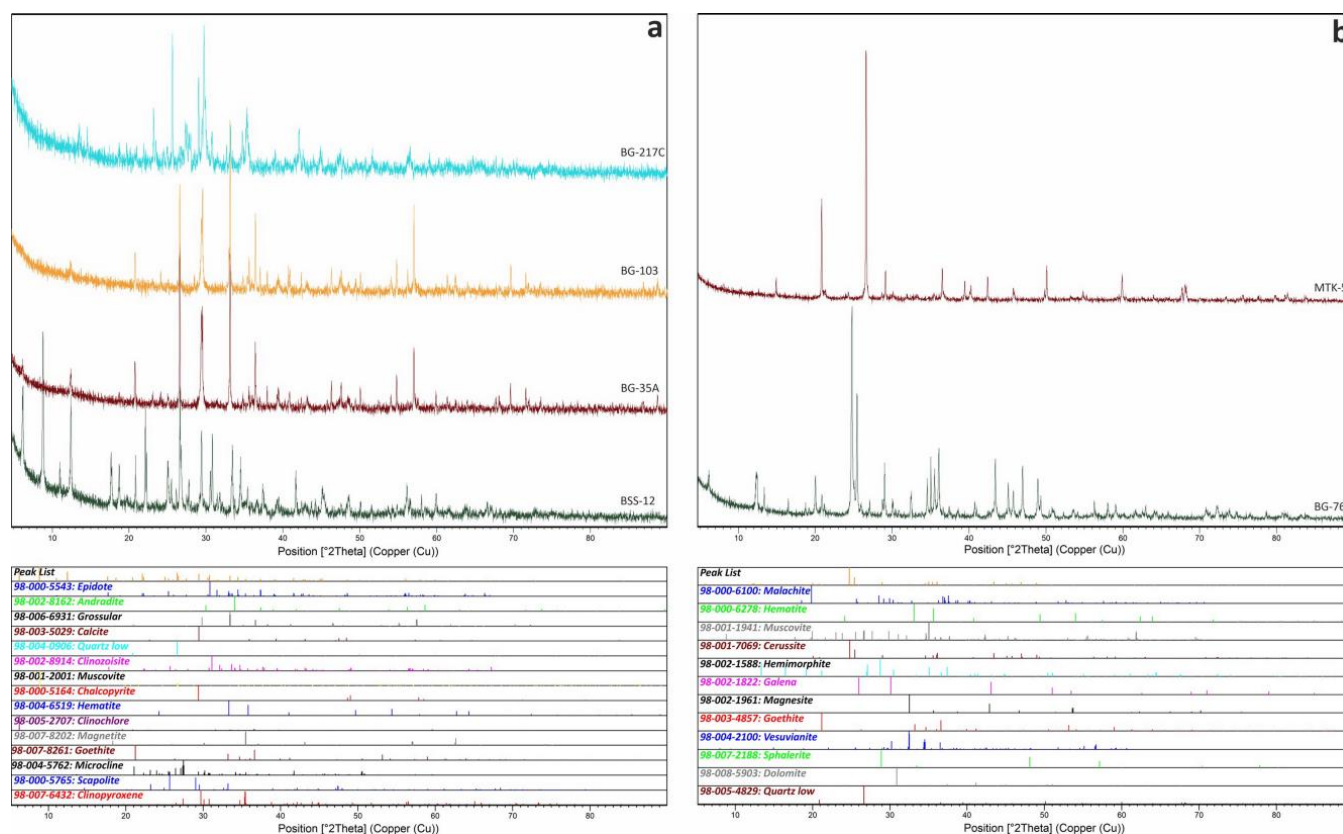


Figure 11. XRD patterns of some selected altered samples collected from the different skarn zones: (a) Intermediate exoskarn zones. (b) Distal exoskarn zones.

Table 1. Major, trace, and rare earth elements (REE) of the Yolindi metagranodiorite, Şaroluk granitoids, and Torasan Formation rocks of the Yolindi area.

	Yolindi Metagranodiorite (<i>n</i> = 5)			Şaroluk Granitoid (<i>n</i> = 22)			Torasan Formation (<i>n</i> = 13)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
SiO ₂	65.68	72.98	68.57	56.00	63.17	61.11	32.48	73.87	55.98
Al ₂ O ₃	12.42	15.71	14.50	15.34	17.48	16.08	5.79	16.33	13.10
Fe ₂ O ₃	3.32	4.98	4.06	3.33	6.60	4.60	2.63	23.80	8.02
MgO	0.65	1.52	1.15	1.97	3.59	2.53	0.68	8.79	3.08
CaO	1.20	3.33	1.82	4.68	6.85	5.41	0.64	22.23	8.05
Na ₂ O	2.76	4.81	3.70	3.08	3.69	3.32	0.01	3.31	1.84
K ₂ O	1.59	4.41	3.47	3.73	4.94	4.46	0.72	5.94	2.65
TiO ₂	0.35	0.60	0.51	0.58	0.85	0.67	0.31	1.07	0.68
P ₂ O ₅	0.09	0.19	0.15	0.26	0.40	0.31	0.09	0.36	0.16
MnO	0.03	0.12	0.07	0.05	0.14	0.09	0.01	1.42	0.23
Cr ₂ O ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.30	0.04
SO ₃	0.01	0.21	0.05	0.01	1.05	0.07	0.01	8.93	2.10
Cl	0.01	0.14	0.07	0.07	0.26	0.15	0.01	0.95	0.16
LOI	1.21	2.13	1.77	0.53	1.77	0.97	1.37	10.63	3.77
<i>Trace and rare earth elements (REE)</i>									
Ag	0.4	0.7	0.5	0.3	0.8	0.5	0.0	3.5	0.4
As	1.0	15.0	8.2	5.0	24.0	13.5	1.0	214.0	53.3
Au	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.5	0.1
Ba	297.0	843.0	585.2	618.0	1119.0	917.3	46.0	1539.0	447.7
Be	1.9	2.9	2.4	3.2	4.7	3.8	1.2	4.7	2.4
Bi	0.0	0.1	0.1	0.1	1.4	0.4	0.1	7.7	1.7
Cd	0.2	7.0	2.0	0.0	12.8	1.9	0.3	12.2	3.9
Co	14.0	21.0	17.3	13.0	38.0	25.2	3.0	55.0	26.5
Cs	1.6	3.8	3.0	3.4	8.7	6.0	0.9	12.1	4.9
Cu	1.0	10.0	4.0	1.0	98.0	26.4	9.0	71.0	31.6
Ga	15.8	25.3	18.2	14.1	21.4	18.0	11.2	27.2	17.2
Hf	1.9	2.2	2.1	0.0	0.5	0.1	0.1	2.5	1.0
Li	15.7	25.6	20.2	5.3	51.0	22.5	10.3	39.5	21.8
Mo	0.4	2.3	1.1	0.6	10.4	2.5	0.0	46.4	6.9
Nb	8.0	18.0	12.0	13.0	20.0	16.3	2.0	19.0	11.8
Ni	8.0	16.0	11.0	12.0	24.0	14.8	23.0	313.0	83.0
Pb	1.0	69.0	19.7	17.0	875.0	72.5	1.0	38.0	11.4
Rb	66.0	154.0	105.7	124.0	183.8	146.9	28.7	211.4	92.2
S	40.1	846.9	193.7	40.1	4220.4	264.1	40.0	35,761.0	8417.5
Sb	0.4	0.8	0.6	0.2	1.2	0.7	0.0	37.9	6.2
Sn	1.1	2.8	1.9	0.5	2.3	0.9	0.4	19.9	5.1
Sr	132.0	402.0	221.5	494.0	687.0	576.7	148.0	408.0	236.5
Tl	0.2	1.1	0.6	0.6	1.2	0.9	0.2	1.1	0.7
V	29.0	61.0	42.5	61.0	130.0	80.2	40.0	224.0	88.1
W	100.0	183.0	148.5	75.0	360.0	186.0	19.0	359.0	99.2
U	2.3	11.9	4.3	5.0	17.0	10.1	0.3	3.5	1.8
Zn	32.0	59.0	44.7	15.0	180.0	55.2	11.0	577.0	96.3
Zr	115.0	188.0	161.5	141.0	190.0	163.7	75.0	231.0	165.2
Sc	8.0	16.0	11.0	7.0	22.0	12.8	7.0	39.0	14.8
Y	11.2	25.5	20.9	16.4	27.4	21.7	8.9	39.2	21.0
La	20.4	41.3	28.0	33.3	50.8	44.2	6.5	51.7	24.3
Ce	38.6	71.9	53.1	62.3	99.9	85.0	12.6	95.2	48.7
Pr	4.4	7.2	5.9	7.2	11.3	9.5	1.5	11.0	5.7
Nd	16.4	24.4	21.4	27.0	41.4	34.8	6.1	40.2	21.5
Sm	3.6	5.2	4.6	5.3	8.1	6.9	2.0	7.4	4.5
Eu	1.0	1.3	1.1	1.6	2.0	1.8	0.9	2.0	1.3
Gd	3.2	4.7	4.0	4.2	6.7	5.5	1.5	7.4	4.5
Tb	0.5	0.8	0.7	0.5	1.0	0.8	0.2	1.2	0.7

Table 1. Cont.

	Yolindi Metagranodiorite (n = 5)			Şaroluk Granitoid (n = 22)			Torasan Formation (n = 13)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
Dy	2.3	4.5	3.8	2.7	5.2	4.1	1.4	6.7	3.9
Ho	0.5	0.9	0.8	0.5	0.9	0.8	0.3	1.4	0.8
Er	1.3	2.8	2.3	1.5	2.8	2.3	0.8	4.2	2.2
Tm	0.2	0.4	0.3	0.2	0.4	0.3	0.1	0.5	0.3
Yb	1.4	2.8	2.3	1.5	2.7	2.2	0.7	3.4	1.9
Lu	0.2	0.4	0.3	0.2	0.4	0.3	0.1	0.5	0.3
Th	7.1	39.5	15.5	19.2	40.2	29.5	0.3	15.0	7.9
Zr	115.0	188.0	161.5	141.0	190.0	163.7	75.0	231.0	165.2
Sr	132.0	402.0	221.5	494.0	687.0	576.7	148.0	408.0	236.5
Th	7.1	39.5	15.5	19.2	40.2	29.5	0.3	15.0	7.9
Sc	8.0	16.0	11.0	7.0	22.0	12.8	7.0	39.0	14.8
Y	11.2	25.5	20.9	16.4	27.4	21.7	8.9	39.2	21.0
La	20.4	41.3	28.0	33.3	50.8	44.2	6.5	51.7	24.3
Ce	38.6	71.9	53.1	62.3	99.9	85.0	12.6	95.2	48.7
Pr	4.4	7.2	5.9	7.2	11.3	9.5	1.5	11.0	5.7
Nd	16.4	24.4	21.4	27.0	41.4	34.8	6.1	40.2	21.5
Sm	3.6	5.2	4.6	5.3	8.1	6.9	2.0	7.4	4.5
Eu	1.0	1.3	1.1	1.6	2.0	1.8	0.9	2.0	1.3
Gd	3.2	4.7	4.0	4.2	6.7	5.5	1.5	7.4	4.5
Tb	0.5	0.8	0.7	0.5	1.0	0.8	0.2	1.2	0.7
Dy	2.3	4.5	3.8	2.7	5.2	4.1	1.4	6.7	3.9
Ho	0.5	0.9	0.8	0.5	0.9	0.8	0.3	1.4	0.8
Er	1.3	2.8	2.3	1.5	2.8	2.3	0.8	4.2	2.2
Tm	0.2	0.4	0.3	0.2	0.4	0.3	0.1	0.5	0.3
Yb	1.4	2.8	2.3	1.5	2.7	2.2	0.7	3.4	1.9
Lu	0.2	0.4	0.3	0.2	0.4	0.3	0.1	0.5	0.3
<i>Parameters</i>									
FeO*(Total)	2.99	4.48	3.65	3.00	5.94	4.14	2.37	21.42	7.22
Na ₂ O + K ₂ O	6.40	7.84	7.17	6.90	8.12	7.79			
A/CNK	0.97	1.23	1.11	0.71	0.91	0.80			
A/NK	1.33	1.63	1.47	1.48	1.80	1.56			
FeO* + MnO	3.05	4.60	3.73	3.07	6.04	4.23			
Fe ₂ O ₃ + TiO ₂	3.67	5.58	4.57	3.91	7.40	5.27			
ΣREE	98.74	159.26	128.67	148.13	228.03	198.41	41.56	230.95	120.50
ΣLREE	84.50	149.68	114.10	136.82	207.91	182.22	29.69	207.00	105.98
ΣHREE	9.58	16.77	14.57	11.31	20.12	16.19	5.12	25.32	14.51
(La/Yb) _N	5.16	19.76	8.93	11.16	16.45	13.69	2.13	16.84	9.21
(La/Sm) _N	2.72	5.27	3.72	3.30	4.71	3.97	2.04	4.27	3.11
(Gd/Yb) _N	1.09	1.82	1.42	1.79	2.31	2.02	1.16	3.81	2.08
(Tb/Yb) _N	1.08	1.66	1.33	1.38	2.01	1.73	1.23	3.13	1.83
Eu/Eu*	0.74	1.02	0.83	0.77	1.06	0.92	0.53	2.11	1.02
K wt%							0.60	4.93	2.20
K (ppm)							5977.09	49,310.97	22,011.78
K/Rb (ppm)							143.28	315.92	228.95
Function 1							−7.70	12.62	1.77
Function 2							−8.06	5.03	−1.15

In comparison to HREE (which averages 14.3 ppm and 16.2 ppm for Yolindi metagranodiorites and Şaroluk granitoids, respectively), all samples of the studied granitoid rocks are highly enriched in LREE (average values of 112.3 ppm and 182.2 ppm for Yolindi metagranodiorites and Şaroluk granitoids, respectively) (Table 1). The chondrite-normalized REE patterns of these rock units also show enriched LREE relative to the HREE (Figure 12g), with an average of (La/Yb)_N = 9.1 and 13.7, (La/Sm)_N = 3.6 and 3.9, (Gd/Yb)_N = 1.5 and 2.0, and (Tb/Yb)_N = 1.4 and 1.7 for Yolindi metagranodiorites and Şaroluk granitoids, respectively (Table 1). The Eu-negative anomalies of the Yolindi metagranodiorite and

Şaroluk granitoid samples with an average of $\text{Eu}/\text{Eu}^* = 0.85$ and 9.2 indicate that they formed during differentiation [55] (Figure 12g). The primitive mantle-normalized immobile element profiles of the studied granitoid rocks [55] (Figure 12h) reveal depletion in Ba, Nb, Sr, P, Zr, Eu, and Ti relative to Th-U, K, and La-Pb, compatible with a subduction-associated petrogenesis [56]. The upper continental crust (UCC)-normalized REE pattern of these rocks displays flat behavior [57] (Figure 12i), typically less than one, indicating that these rocks are mainly compatible with the UCC compositions.

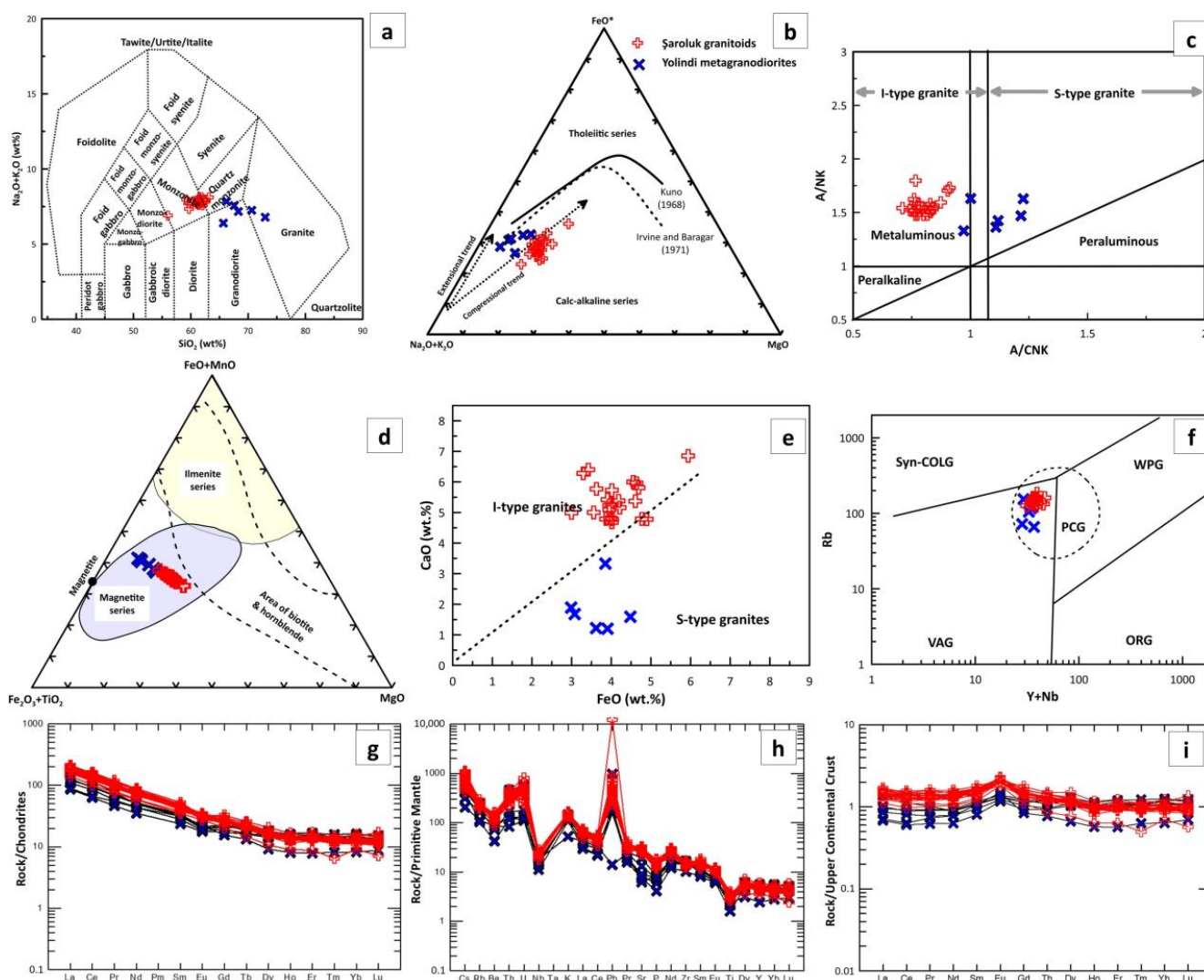


Figure 12. Geochemical diagrams of the Yolindi metagranodiorite and Şaroluk granitoid rocks. (a) TAS classification diagram of Middlemost [49]. (b) AFM diagram [50,52]. Trends of compressional and extensional environments according to Petro et al. Kuno [51]. (c) Alumina saturation index (ASI) in the investigated granitoid rocks. $\text{ASI} = 1$ from Shand [53], $\text{ASI} = 1.1$ from Chappell and White [58]. (d) $\text{Fe}_2\text{O}_3 + \text{TiO}_2$ – $\text{FeO} + \text{MnO}$ – MgO diagram according to Ishihara [54]. (e) CaO vs. FeO^t diagram according to Chappell and White [59]. (f) Rb vs. $(\text{Y} + \text{Nb})$ tectonic discrimination diagram, modified according to Pearce, et al. [60] and Pearce [61]. (g) Chondrite-normalized REE patterns [55]. (h) Primitive mantle-normalized trace element patterns [55]. (i) Upper continental crust (UCC)-normalized REEs [57].

5.2.2. Geochemistry of the Torasan Formation

The major, trace, and rare earth element (REE) contents of 13 representative samples collected from the unaltered metatuffs, metasediments, and schists of the Torasan Formation are analyzed (Table 1). The original chemical composition of the Torasan Formation

reveals that the source area was primarily quartz diorite, granodiorite, and granitic in composition, with minor quantities of basalt and andesite (Figure 13a). With a range of 143.3 to 315.9 and an average of 228, the K/Rb ratio (Table 1) of the Torasan Formation reveals that these rocks have acidic/intermediate features and are derived from metavolcanic tuffs, metagreywackes, and arkosic sands [62] from the upper continental crusts (Figure 13b,c). Based on the Function1–Function2 classification diagram of Roser and Korsch [63], the compositional characteristics of the studied rocks are mostly comparable to the P4-quartzose sedimentary provenance and P1-mafic-igneous provenance, with a few P3-felsic magmatic suites (Figure 13d). They formed predominantly as a result of recycling from old sedimentary rocks derived from highly weathered mafic and felsic terrains. The La/Th–Hf diagram reveals that the investigated metatuff samples originated from a mixed felsic/basic and less andesitic continental magmatic arc analogous to the average upper continental crust, with low/intermediate La/Th ratios ranging from 1.1 to 24.4 with an average of 4.8 and Hf levels ranging from 0.1 to 2.5 ppm with an average of 1.0 ppm (Figure 13e). They exhibit low total rare earth element levels (ΣREE) (up to 230.9 ppm with an average of 120.9 ppm), $(\text{La}/\text{Yb})_{\text{N}} = 2.1\text{--}16.8$ ppm, $(\text{Gd}/\text{Yb})_{\text{N}} = 1.2\text{--}3.8$ ppm, and a positive Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.53\text{--}2.11$ ppm) that are comparable to the upper continental crust (UCC) of Taylor and McLennan [57] (Figure 13f).

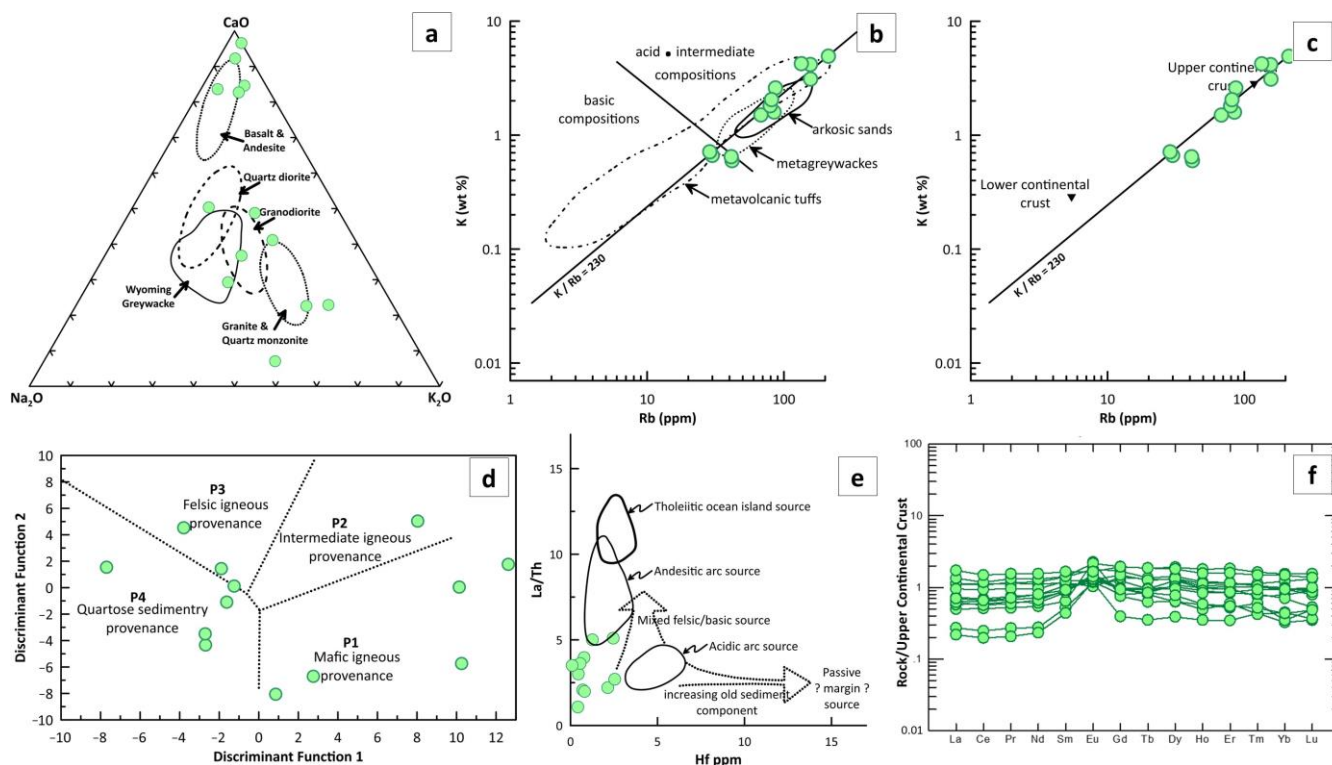


Figure 13. Geochemical diagrams of the Torasan Formation rocks. (a) CaO–Na₂O–K₂O composition diagram according to Condie, et al. [64]. (b,c) K–Rb diagrams according to Floyd and Leveridge [62]. Fields of unmetamorphosed arkosic sands according to van de Kamp, et al. [65]; low–grade metagreywackes according to Condie, et al. [64] and Caby, et al. [66]; and higher-grade metavolcanic tuffs according to van de Kamp [67]. (d) Plot of samples in discriminant functions F1 vs. F2; provenance fields are according to Roser and Korsch [63]. (e) Hf vs. La/Th according to Floyd and Leveridge [62]. (f) Upper continental crust (UCC)–normalized REE patterns of Taylor and McLennan [57].

5.3. Alteration Geochemistry

New alteration minerals have replaced the primary ones, and various ores (Fe, Cu, Pb, Zn, W, Au, ... etc.) have precipitated in the Yolindi Fe–Cu skarn deposit due to the complex interactions between the magmatic hydrothermal fluids extracted during the magmatic intrusion of the Şaroluk pluton with the surrounding Torasan Formation, as

well as the metamorphic conditions. Table 2 shows the geochemical characteristics of the hydrothermal skarn zonation based on the different elements' concentrations from the chemical analyses (XRF and ICP-MS). The analyzed samples from the different zones have different signatures, according to the different diagrams of the different alteration indices (Figure 14), which aid in visualizing the effects on SiO₂, FeO, MgO, CaO, Na₂O, and K₂O resulting from the metasomatic alteration compared to the unaltered protoliths [68].

Table 2. Major, trace, and rare earth elements (REE) of the different skarn zones of the Yolindi area.

	Endoskarn (n = 8)			Proximal (n = 34)			Intermediate (n = 45)			Distal (n = 14)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
SiO ₂	7.52	63.49	31.13	1.48	73.25	31.08	0.51	77.50	41.21	0.41	81.08	48.27
Al ₂ O ₃	1.02	27.47	10.60	0.12	5.71	1.90	0.12	28.62	9.55	0.07	27.72	4.88
Fe ₂ O ₃	4.13	82.81	42.43	5.49	97.52	28.09	0.06	60.00	16.74	0.06	62.58	22.81
MgO	0.05	2.26	0.70	0.07	11.86	2.54	0.01	9.00	2.68	0.01	2.07	0.32
CaO	0.42	20.07	4.55	0.12	37.96	22.19	0.12	55.41	17.71	0.04	54.97	10.05
Na ₂ O	0.01	0.84	0.27	0.01	0.06	0.01	0.01	2.76	0.46	0.01	0.06	0.02
K ₂ O	0.01	3.29	0.75	0.01	0.14	0.02	0.01	8.67	1.18	0.01	2.31	0.29
TiO ₂	0.08	1.25	0.53	0.01	0.41	0.04	0.01	1.63	0.47	0.01	0.33	0.08
P ₂ O ₅	0.01	1.17	0.23	0.01	0.14	0.02	0.01	0.62	0.13	0.01	0.15	0.04
MnO	0.05	0.75	0.22	0.09	1.57	0.69	0.02	1.91	0.53	0.01	3.87	0.69
Cr ₂ O ₃	0.01	0.66	0.10	0.01	0.64	0.09	0.01	0.38	0.03	0.01	0.71	0.07
SO ₃	0.01	14.01	1.93	0.01	20.14	4.02	0.01	24.45	2.40	0.01	4.23	0.39
Cl	0.01	0.21	0.09	0.01	0.20	0.05	0.01	1.14	0.12	0.01	0.03	0.02
LOI	0.32	15.27	6.33	0.01	22.81	9.19	0.36	43.50	6.30	0.43	44.09	7.90
<i>Trace and rare earth elements (REE)</i>												
Ag	0.3	4.7	1.7	0.0	3.6	0.6	0.0	92.1	3.5	0.0	37.2	7.6
As	10.0	726.0	302.5	2.0	1051.0	157.9	12.0	629.0	140.8	8.0	3158.0	716.6
Au	0.0	0.1	0.0	0.0	1.4	0.1	0.0	0.2	0.0	0.0	0.6	0.2
Ba	10.0	568.0	148.6	1.0	77.0	6.4	1.0	932.0	163.0	1.0	717.0	150.4
Be	0.7	3.0	1.5	0.8	2.8	1.5	0.7	5.6	2.7	1.4	18.7	4.6
Bi	4.5	6.1	5.2	0.1	143.5	6.6	0.2	9.2	2.3	0.6	18,962.4	1420.9
Cd	0.0	2.9	1.3	0.0	11.2	2.4	0.0	14.7	2.5	0.0	500.0	40.3
Co	7.0	409.0	115.1	1.0	124.0	35.2	1.0	73.0	22.2	1.0	785.0	212.6
Cs	0.1	8.6	2.7	0.1	2.6	0.6	0.0	21.5	3.1	0.1	3.9	1.2
Cu	302.0	997.0	663.8	5.0	3006.0	329.3	5.0	5204.0	309.5	2.0	108,032.0	9043.4
Ga	6.0	27.0	14.4	1.9	27.0	8.3	0.5	37.9	16.1	0.0	30.1	10.5
Hf	0.3	1.0	0.7	0.0	1.5	0.1	0.0	5.2	0.9	0.0	1.3	0.2
In	0.2	3.2	1.0	0.0	0.7	0.1	0.0	3.8	0.6	0.0	4.6	1.3
Ir	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Li	1.6	33.2	12.7	2.5	32.2	17.8	6.4	89.4	22.3	0.5	78.7	19.3
Mo	1.0	66.0	27.5	1.0	27.0	7.1	1.0	240.0	12.4	1.0	167.0	25.6
Nb	2.0	23.0	10.3	1.0	8.0	2.4	1.0	22.0	8.9	1.0	8.0	2.4
Ni	28.0	332.0	165.5	49.0	397.0	127.1	1.0	395.0	99.0	1.0	326.0	119.4
Pb	1.0	130.0	47.9	1.0	170.0	17.9	1.0	51,354.0	3119.9	1.0	288,443.0	22,974.3
Rb	3.5	126.2	35.2	1.4	13.3	8.3	0.9	319.1	48.8	1.0	85.1	20.3
S	40.0	56,104.3	7730.1	40.0	80,659.9	16,098.4	40.0	97,921.3	9618.2	40.0	16,941.0	1566.9
Sb	1.2	37.8	10.3	0.7	18.0	4.2	0.0	63.8	6.3	0.1	230.5	36.7
Sn	1.7	68.4	16.5	0.3	13.6	2.5	0.0	189.0	14.5	0.4	121.6	13.9
Sr	9.0	203.0	68.9	5.0	166.0	72.4	6.0	955.0	179.0	1.0	154.0	50.8
Te	0.0	7.5	2.1	0.0	7.5	0.9	0.0	17.2	1.9	0.0	61.0	6.7
Tl	0.0	0.8	0.3	0.0	0.2	0.0	0.0	2.5	0.5	0.0	10.4	2.1
V	16.0	120.0	56.6	1.0	41.0	14.2	1.0	170.0	60.6	1.0	79.0	19.5
W	14.0	217.0	81.9	5.0	327.0	143.5	6.0	280.0	111.5	6.0	557.0	198.6
U	3.2	16.1	10.4	0.0	1.9	0.3	0.1	7.3	1.7	0.1	14.5	2.5
Zn	16.0	383.0	88.6	17.0	305.0	110.6	5.0	12,778.0	638.4	1.0	104,169.0	8047.6
Zr	26.0	306.0	128.6	12.0	152.0	21.8	15.0	296.0	110.5	14.0	789.0	93.9
Sc	1.0	29.0	9.9	1.0	14.0	5.8	1.0	32.0	12.4	1.0	18.0	4.1
Y	0.8	31.3	15.2	1.1	11.5	3.4	0.2	54.6	16.1	0.5	37.8	7.8

Table 2. Cont.

	Endoskarn (n = 8)			Proximal (n = 34)			Intermediate (n = 45)			Distal (n = 14)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
La	5.5	368.4	64.6	0.0	18.2	1.3	0.0	63.2	18.6	0.0	87.1	9.7
Ce	7.6	432.5	103.3	0.1	35.1	2.3	0.1	126.2	37.0	0.1	50.6	10.2
Pr	0.6	33.6	9.0	0.0	3.7	0.3	0.0	14.5	4.6	0.0	14.4	2.1
Nd	1.3	98.1	30.6	0.0	12.4	1.1	0.0	56.0	18.0	0.0	51.0	8.0
Sm	0.1	11.9	4.9	0.0	2.1	0.3	0.0	10.7	3.7	0.0	9.6	1.8
Eu	0.0	2.4	1.1	0.0	0.2	0.1	0.0	3.2	1.1	0.0	10.3	1.3
Gd	0.1	9.5	4.0	0.0	2.5	0.4	0.0	10.1	3.5	0.0	9.1	1.6
Tb	0.0	1.4	0.6	0.0	0.4	0.1	0.0	1.6	0.5	0.0	1.6	0.3
Dy	0.1	6.6	3.1	0.0	2.1	0.4	0.0	9.9	3.0	0.0	8.7	1.4
Ho	0.0	1.2	0.6	0.0	0.4	0.1	0.0	1.8	0.6	0.0	1.8	0.3
Er	0.1	3.4	1.6	0.0	1.2	0.2	0.0	5.1	1.6	0.0	5.3	0.8
Tm	0.0	0.5	0.2	0.0	0.2	0.0	0.0	0.6	0.2	0.0	0.8	0.1
Yb	0.0	3.0	1.4	0.0	1.3	0.2	0.0	4.2	1.4	0.0	5.1	0.7
Lu	0.0	0.5	0.2	0.0	0.2	0.0	0.0	0.5	0.2	0.0	0.7	0.1
Th	0.0	28.6	7.6	0.0	3.6	0.4	0.0	16.7	5.0	0.0	7.8	1.7
Zr	26.0	306.0	128.6	12.0	152.0	21.8	15.0	296.0	110.5	14.0	789.0	93.9
Sr	9.0	203.0	68.9	5.0	166.0	72.4	6.0	955.0	179.0	1.0	154.0	50.8
Th	0.0	28.6	7.6	0.0	3.6	0.4	0.0	16.7	5.0	0.0	7.8	1.7
Sc	1.0	29.0	9.9	1.0	14.0	5.8	1.0	32.0	12.4	1.0	18.0	4.1
Y	0.8	31.3	15.2	1.1	11.5	3.4	0.2	54.6	16.1	0.5	37.8	7.8
La	5.5	368.4	64.6	0.0	18.2	1.3	0.0	63.2	18.6	0.0	87.1	9.7
Ce	7.6	432.5	103.3	0.1	35.1	2.3	0.1	126.2	37.0	0.1	50.6	10.2
Pr	0.6	33.6	9.0	0.0	3.7	0.3	0.0	14.5	4.6	0.0	14.4	2.1
Nd	1.3	98.1	30.6	0.0	12.4	1.1	0.0	56.0	18.0	0.0	51.0	8.0
Sm	0.1	11.9	4.9	0.0	2.1	0.3	0.0	10.7	3.7	0.0	9.6	1.8
Eu	0.0	2.4	1.1	0.0	0.2	0.1	0.0	3.2	1.1	0.0	10.3	1.3
Gd	0.1	9.5	4.0	0.0	2.5	0.4	0.0	10.1	3.5	0.0	9.1	1.6
Tb	0.0	1.4	0.6	0.0	0.4	0.1	0.0	1.6	0.5	0.0	1.6	0.3
Dy	0.1	6.6	3.1	0.0	2.1	0.4	0.0	9.9	3.0	0.0	8.7	1.4
Ho	0.0	1.2	0.6	0.0	0.4	0.1	0.0	1.8	0.6	0.0	1.8	0.3
Er	0.1	3.4	1.6	0.0	1.2	0.2	0.0	5.1	1.6	0.0	5.3	0.8
Tm	0.0	0.5	0.2	0.0	0.2	0.0	0.0	0.6	0.2	0.0	0.8	0.1
Yb	0.0	3.0	1.4	0.0	1.3	0.2	0.0	4.2	1.4	0.0	5.1	0.7
Lu	0.0	0.5	0.2	0.0	0.2	0.0	0.0	0.5	0.2	0.0	0.7	0.1
<i>Parameters</i>												
FeO (Total)	3.72	74.53	38.18	4.94	87.77	25.28	0.05	54.00	15.07	0.05	56.32	20.53
Ishikawa AI	1.08	58.26	24.28	0.88	72.28	15.93	0.11	94.88	28.38	0.60	94.92	40.17
AAAI	11.83	73.61	43.96	4.66	76.45	15.72	0.09	90.54	24.68	0.07	97.68	65.84
A' index	23.16	84.79	52.01	6.28	97.87	29.96	0.16	61.14	24.65	0.11	66.78	27.37
F index	4.78	75.10	39.10	7.28	88.10	28.52	0.40	54.33	18.28	0.41	56.79	21.54
C index	0.42	20.07	4.55	0.12	37.96	22.19	0.12	55.41	17.71	0.04	54.97	10.05
A index	1.01	24.81	9.85	0.11	5.64	1.88	0.11	26.61	8.36	0.06	27.52	4.58
M index	0.05	2.26	0.70	0.07	11.86	2.54	0.01	9.00	2.68	0.01	2.07	0.32

Endoskarn, proximal, intermediate, and distal skarn zones exhibit SiO₂ contents that are lower than those of Şaroluk quartz monzonite (an average of 61.1 wt.%) and the Torasan Formation (an average of 56.0 wt.%), with averages of 31.1, 31.0, 41.2, and 48.3 wt.%, respectively (Table 2). However, the average Fe₂O₃ and CaO contents of the endoskarn, proximal, intermediate, and distal skarn zones are higher than those of the Şaroluk quartz monzonite (Fe₂O₃ = 4.6 wt.% and CaO = 5.4 wt.%) and Torasan Formation (Fe₂O₃ = 8.0 wt.% and CaO = 8.0 wt.%), with averages of Fe₂O₃ = 42.4 wt.% and CaO = 4.5 wt.%, Fe₂O₃ = 28.1 wt.% and CaO = 22.2 wt.%, Fe₂O₃ = 16.7 wt.% and CaO = 17.7 wt.%, and Fe₂O₃ = 22.8 wt.% and CaO = 10.0 wt.%, respectively (Table 2). The samples from these four skarn zones have a lower value in the alteration index (AI) from Ishikawa, et al. [69] and exhibit clustering and sifting towards the field of the calcite and epidote when plotting the advanced argillic

alteration index (AAAI) of Williams and Davidson [70] vs. the AI diagram, revealing that this alteration zone was paired with alkali removal with CaO enrichment, with the exception of some samples from distal zones that have sericite, kaolinite, and pyrophyllite alteration (Figure 14a). The A'CF diagram by Bonnet and Corriveau [71] is particularly useful for illustrating carbonate (Ca) or propylitic alteration (Ca-Fe), which is distinguished by noteworthy contents of calcic minerals (calcite, epidote, grossular, anorthite, and/or diopside), confined near to apex C, indicating the proximal and intermediate zones, except the endoskarn and distal, which have slightly advanced argillic signatures (Figure 14b). The advanced argillic-siliceous (Al-Si), argillic-iron (Al-Fe), and chloritic (Mg-Fe) alteration vectors all point towards the apices A, F, and M, respectively, in the AFM diagram (Figure 14c) [71]. The studied samples of the skarn zones cluster mostly toward the F apex, showing that magnetite, hematite, iron sulfides, and, in some instances, garnet dominate iron-bearing alteration (Figure 14c). Sericitic- or potassic-alteration types, including a few samples of endoskarn and distal zones, rarely ever plot towards apex A (Figure 14c).

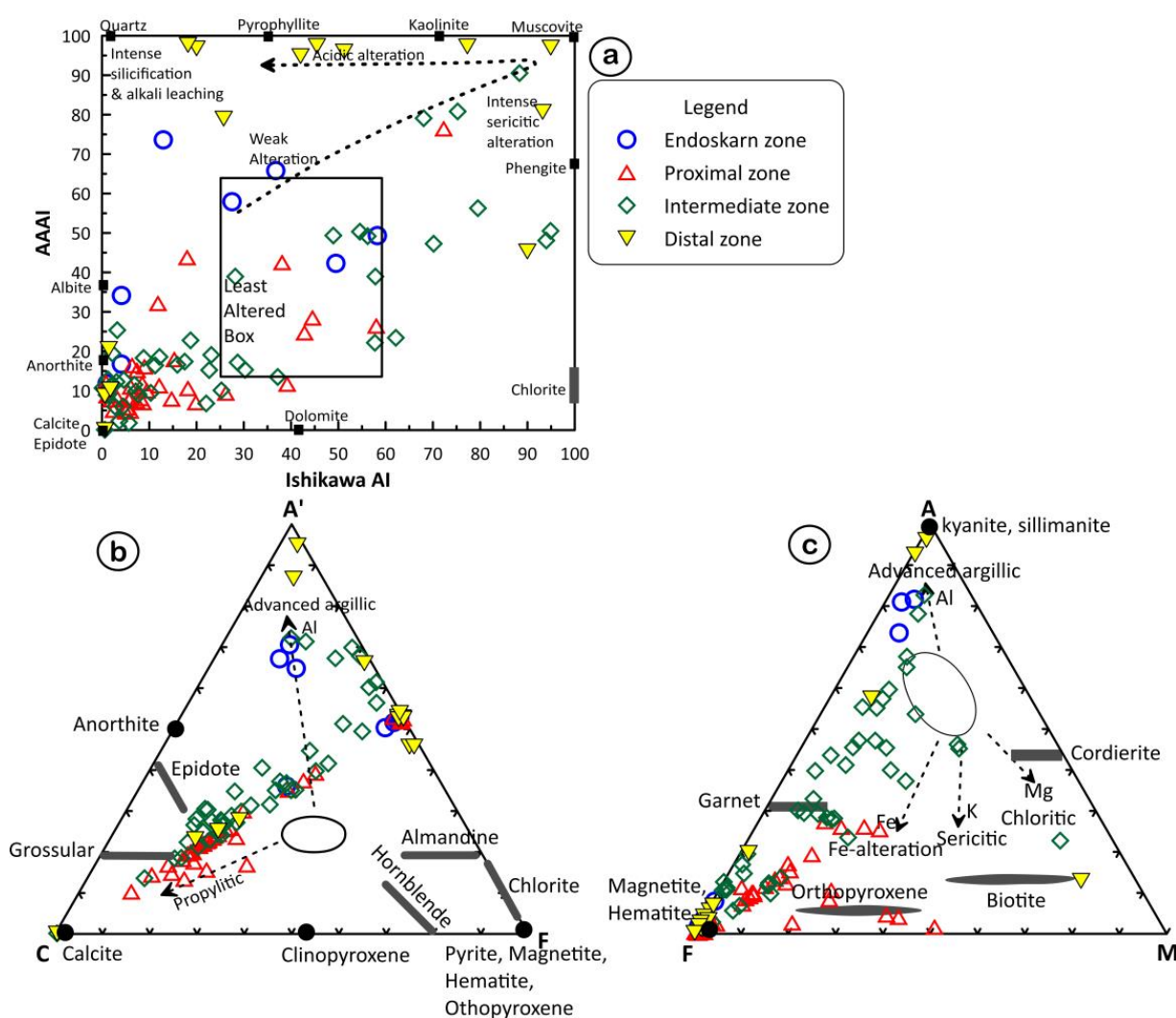


Figure 14. (a) AAAI vs. AI diagram according to Williams and Davidson [70] and Bonnet, et al. [72], AAAI (advanced argillic alteration index according to Williams and Davidson [70]) = $100 \times \text{SiO}_2 / [\text{SiO}_2 + (10 \times \text{MgO}) + (10 \times \text{CaO}) + (10 \times \text{Na}_2\text{O})]$ and AI (alteration index of Ishikawa, et al. [69]) = $100 \times [(K_2O + MgO) / (K_2O + MgO + Na_2O + CaO)]$. (b) A'CF Ternary diagram (A' = Al₂O₃ + Fe₂O₃ - (K₂O + Na₂O), C = CaO, F = FeO + MnO + MgO) according to Bonnet and Corriveau [71]. (c) AFM Ternary diagram (A = Al₂O₃ - K₂O, F = FeO, M = MgO) according to Bonnet and Corriveau [71].

5.4. Mineral Chemistry

The representative minerals that were selected from the different skarn zonations in the Yolindi area, e.g., garnet, clinopyroxene, scapolite, plagioclase, epidote, biotite, chlorite, sericite, calcic amphibole, carbonate (calcite and cerussite), magnetite, hematite, and sulfide (pyrite, chalcopyrite, and galena), were analyzed with an electron microprobe (Tables 3–14).

Table 3. Representative electron microprobe data of garnet from different skarn zones of the Yolindi Cu-Fe skarn deposit.

Dataset	Endoskarn (<i>n</i> = 12)			Proximal Prograde (<i>n</i> = 35)			Proximal Retrograde (<i>n</i> = 21)			Intermediate Retrograde/Andradite (<i>n</i> = 11)			Intermediate Retrograde/Andradite-Grossular (<i>n</i> = 27)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
SiO ₂	29.2	33.8	31.9	29.5	39.3	33.6	27.2	34.7	31.4	30.4	35.9	33.3	32.0	39.8	35.6
TiO ₂	0.3	0.4	0.4	0.0	0.0	0.0	0.0	1.6	0.6	0.0	0.5	0.1	0.0	0.6	0.2
Al ₂ O ₃	4.0	5.8	4.6	0.0	0.5	0.1	0.0	12.5	8.7	0.1	13.0	3.5	0.1	23.9	11.7
Fe ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
FeO	24.4	36.9	27.8	27.4	31.5	29.3	13.9	28.9	25.6	14.0	30.7	26.3	12.1	35.9	19.7
MnO	0.0	1.5	0.7	0.0	1.3	0.2	0.0	0.6	0.2	0.0	0.0	0.0	0.0	1.4	0.4
MgO	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.2	0.1
CaO	28.2	38.2	34.5	30.1	38.7	36.1	29.0	37.9	32.4	33.2	40.0	36.2	27.1	38.5	31.8
Total	98.7	101.0	100.0	97.5	101.0	99.3	98.0	100.3	98.8	98.4	100.1	99.4	98.1	100.9	99.4
<i>Calculated cations based on 12 oxygen</i>															
<i>Cations</i>															
Si	2.5	2.7	2.6	2.4	3.2	2.8	2.2	2.7	2.6	2.4	3.0	2.7	2.5	3.2	2.8
Ti	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Al	0.4	0.6	0.4	0.0	0.1	0.0	0.0	1.2	0.8	0.0	1.2	0.3	0.0	2.2	1.1
Fe ³⁺	2.1	2.7	2.3	1.5	3.2	2.4	1.3	2.7	2.0	1.7	2.9	2.2	0.4	2.3	1.2
Fe ²⁺	0.0	0.0	0.0	0.0	0.5	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.6	0.3
Mn	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Ca	2.5	3.3	3.0	2.7	3.4	3.2	2.5	3.3	2.8	2.9	3.4	3.2	2.3	3.3	2.7
Fe + Mn	2.2	2.7	2.4	2.1	3.2	2.6	1.3	2.7	2.0	1.7	2.9	2.2	0.8	2.6	1.5
<i>End members</i>															
Almandine	0.0	0.8	0.1	0.0	16.9	3.0	0.0	4.2	0.8	0.0	0.8	0.1	0.0	18.5	8.9
Pyrope	0.0	0.3	0.2	0.0	0.4	0.2	0.0	0.2	0.0	0.0	0.3	0.0	0.0	0.8	0.3
Grossular	12.9	19.2	15.7	0.0	1.9	0.3	0.1	46.5	28.2	0.6	40.4	11.0	0.6	71.0	40.6
Spessartine	0.0	3.3	1.4	0.0	2.5	0.3	0.0	1.6	0.5	0.0	0.0	0.0	0.0	3.7	0.9
Uvarovite	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Andradite	78.6	86.1	81.8	82.7	99.9	96.2	53.4	99.8	69.2	58.2	99.4	88.7	13.0	85.2	48.8

Table 4. Representative electron microprobe data of clinopyroxene from different skarn zones of the Yolindi Cu-Fe skarn deposit.

Dataset	Endoskarn (<i>n</i> = 15)			Exoskarn Proximal (<i>n</i> = 4)			Exoskarn Intermediate (<i>n</i> = 4)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
SiO ₂	51.3	58.0	55.1	52.7	55.3	54.4	51.2	52.9	52.0
TiO ₂	0.1	1.5	0.6	0.0	0.0	0.0	0.0	0.0	0.0
Al ₂ O ₃	0.6	5.1	2.8	0.4	1.2	0.9	0.1	0.3	0.2
Cr ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
FeO	6.7	12.4	9.9	13.6	15.2	14.5	19.8	22.4	20.8
MnO	0.3	2.9	1.9	1.5	2.9	2.3	0.1	0.9	0.4
MgO	15.1	19.2	17.0	13.3	13.9	13.7	4.4	5.8	5.2
CaO	10.3	11.5	10.8	10.5	11.1	10.9	21.6	22.1	21.8
Na ₂ O	0.2	1.3	0.7	0.1	0.1	0.1	0.0	0.1	0.1
K ₂ O	0.0	0.5	0.2	0.0	0.1	0.1	0.0	0.0	0.0
Total	98.2	99.6	99.0	96.0	97.5	96.9	100.0	100.9	100.6

Table 4. Cont.

Dataset	Endoskarn (<i>n</i> = 15)			Exoskarn Proximal (<i>n</i> = 4)			Exoskarn Intermediate (<i>n</i> = 4)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
<i>Calculated cations based on 6 oxygen</i>									
<i>Cations</i>									
Si	1.9	2.2	2.1	2.1	2.2	2.1	2.0	2.1	2.1
Al	0.0	0.2	0.1	0.0	0.1	0.0	0.0	0.0	0.0
Fe + 2	0.2	0.4	0.3	0.4	0.5	0.5	0.6	0.7	0.7
Mn	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.0
Mg	0.8	1.1	0.9	0.8	0.8	0.8	0.3	0.3	0.3
Ca	0.4	0.5	0.4	0.4	0.5	0.5	0.9	0.9	0.9
Na	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
<i>End members</i>									
Wollastonite	24.5	28.4	25.7	25.2	26.9	26.4	47.8	48.5	48.2
Enstatite	50.6	62.0	56.0	44.8	47.2	46.2	13.5	17.8	16.0
Ferrosilite	12.1	23.2	18.3	25.8	28.5	27.4	33.9	38.6	35.8
Diopside	65.5	78.7	72.0	58.2	60.0	59.3	25.7	34.2	30.5
Hedenbergite	15.4	31.1	23.6	32.8	37.1	35.1	64.1	73.2	68.4
Johannsenite	0.8	7.1	4.5	3.6	7.1	5.6	0.3	2.8	1.2
Ti + Cr + Na	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
#Mg	68.5	83.7	75.4	61.1	64.6	62.8	26.0	34.3	30.8

$$\#Mg = 100 \times Mg/[Mg + Fe^{2+}].$$

Table 5. Representative electron microprobe data of scapolite from the intermediate exoskarn zone of the Yolindi Cu-Fe skarn deposit.

Intermediate/Scapolite (<i>n</i> = 7)			
Dataset	Min.	Max.	Av.
SiO ₂	51.7	54.8	53.0
TiO ₂	0.0	0.0	0.0
Al ₂ O ₃	23.5	26.1	25.0
FeO	0.2	0.3	0.2
MnO	0.0	0.0	0.0
MgO	0.0	0.0	0.0
CaO	7.9	12.6	10.5
Na ₂ O	5.6	8.4	7.0
K ₂ O	1.0	1.4	1.3
Cl	2.7	3.5	3.2
F	0.0	0.3	0.2
SO ₃	0.0	0.0	0.0
Total	92.7	107.6	100.4
<i>Formulae based on (Si + Al = 12)</i>			
Si	7.5	8.0	7.7
Al	4.0	4.5	4.3
Total	12.0	12.0	12.0
Fe + 2	0.0	0.0	0.0
Ti	0.0	0.0	0.0
Mg	0.0	0.0	0.0
Mn	0.0	0.0	0.0
Na	1.7	2.5	2.1
Ca	1.3	2.1	1.7
K	0.2	0.3	0.2
Cl	0.6	0.8	0.8
F	0.0	0.1	0.1
S	0.0	0.0	0.0
C *	0.1	0.3	0.2

Table 5. Cont.

Intermediate/Scapolite (<i>n</i> = 7)			
Dataset	Min.	Max.	Av.
Total	16.7	16.9	16.8
%Me **	32.6	52.6	43.0
Al/Al + Si	0.3	0.4	0.4
EqAn ***	34.7	49.2	42.9

Total Fe as FeO. Treatment of total Fe as FeO or Fe₂O₃ produces the same number of Fe atoms in formula, * C calculated by subtraction (Cl + F + S + C = 1.000), ** Me% = 1006 (Ca + Mg + Mn + Fe + Ti)/(Na + K + Ca + Mg + Mn + Fe + Ti), *** EqAn = equivalent anorthite = [100(Al₃)/3] where Al is the Al per formula unit.

Table 6. Representative electron microprobe data of plagioclase from the endoskarn zone of the Yolindi Cu-Fe skarn deposit.

Endoskarn/Plagioclase (<i>n</i> = 13)			
Dataset	Min.	Max.	Av.
SiO ₂	58.0	65.4	61.7
Al ₂ O ₃	21.5	26.1	24.2
FeO	0.1	0.3	0.3
CaO	3.2	7.7	5.3
Na ₂ O	6.6	8.1	7.2
K ₂ O	0.3	0.7	0.5
Total	98.4	99.9	99.2
<i>Calculated cations based on 8 oxygen</i>			
<i>Cations</i>			
Si	2.6	3.0	2.8
Al	1.2	1.4	1.3
Ca	0.2	0.4	0.3
Na	0.6	0.7	0.6
K	0.0	0.0	0.0
<i>End members</i>			
Anorthite	18.0	37.5	27.8
Albite	59.4	79.7	69.0
Orthoclase	1.6	4.6	3.2

- Garnet

Garnet is a coarse-grained mineral that occurs in several skarn zones of the study area, predominantly as zoned andradite with an occasional amount of grossular with intergrowth characteristics. Microscopically, garnet from the endoskarn zone is un-zoned andradite that was partially altered to epidote (Figures 6 and 15a), with high values of SiO₂, FeO, and CaO ranging from 29.2–33.8 wt.%, 24.4–36.9 wt.%, and 28.2–38.2 wt.%, respectively, and a minor amount of Al₂O₃ (an average of 4.6 wt.%) (Table 3). It is mainly andradite in composition, having a range of Adr₇₉Grs₁₃Sps₀Alm₀–Adr₈₆Grs₁₉Sps₃Alm₁ (Table 3). The garnet from the proximal exoskarn zone is zoned andradite in the prograde subzone (Figures 8 and 15b), but in the retrograde subzone, andradite (Fe-rich)–grossular (Al-rich) intergrowth occurs, with compositional change as oscillatory zoning (Figures 8 and 15c). The andradite of the proximal prograde zone has greater SiO₂, FeO, and CaO contents, with an average of 33.6, 29.3, and 36.1, respectively, with an Adr₉₆Alm₃ composition (Table 3). However, the composition of garnet from the proximal retrograde zone shifted from Adr₇₇Grs₂₀Alm₁ (Fe-rich) in its core to Adr₅₉Grs₃₉Alm₁ (Al-rich) in its rim, indicating andradite–grossular intergrowth (Table 3). The garnet from the intermediate zone, on the other hand, represents a variation in composition from entirely andradite to andradite–grossular intergrowth zoning with Adr₈₉Grs₁₁ and Adr₄₉Grs₄₁Alm₉, respectively (Figures 10 and 15d). Andradite has more FeO (an average of 26.3 wt.%) and CaO (an average of 36.2 wt.%) than andradite–grossular, which contains more SiO₂ (an average of 35.6 wt.%) and Al₂O₃ (an average of 11.7 wt.%) (Table 3). Mange and Morton [73] used

the Fe + Mn-Mg-Ca ternary plot to distinguish between various types of garnet, indicating that garnet from the various Yolindi skarn zones is primarily classified as magmatic garnet (Type D), which is typically derived from metasomatic rocks (e.g., skarns), with just a little garnet derived from amphibolite-facies metasedimentary rocks (Type Bii) (Figure 16a). This garnet classification is mostly compatible with garnet from other worldwide Cu-Fe skarn deposits, with a little Zn skarn deposit from Meinert, et al. [1] (Figure 16b).

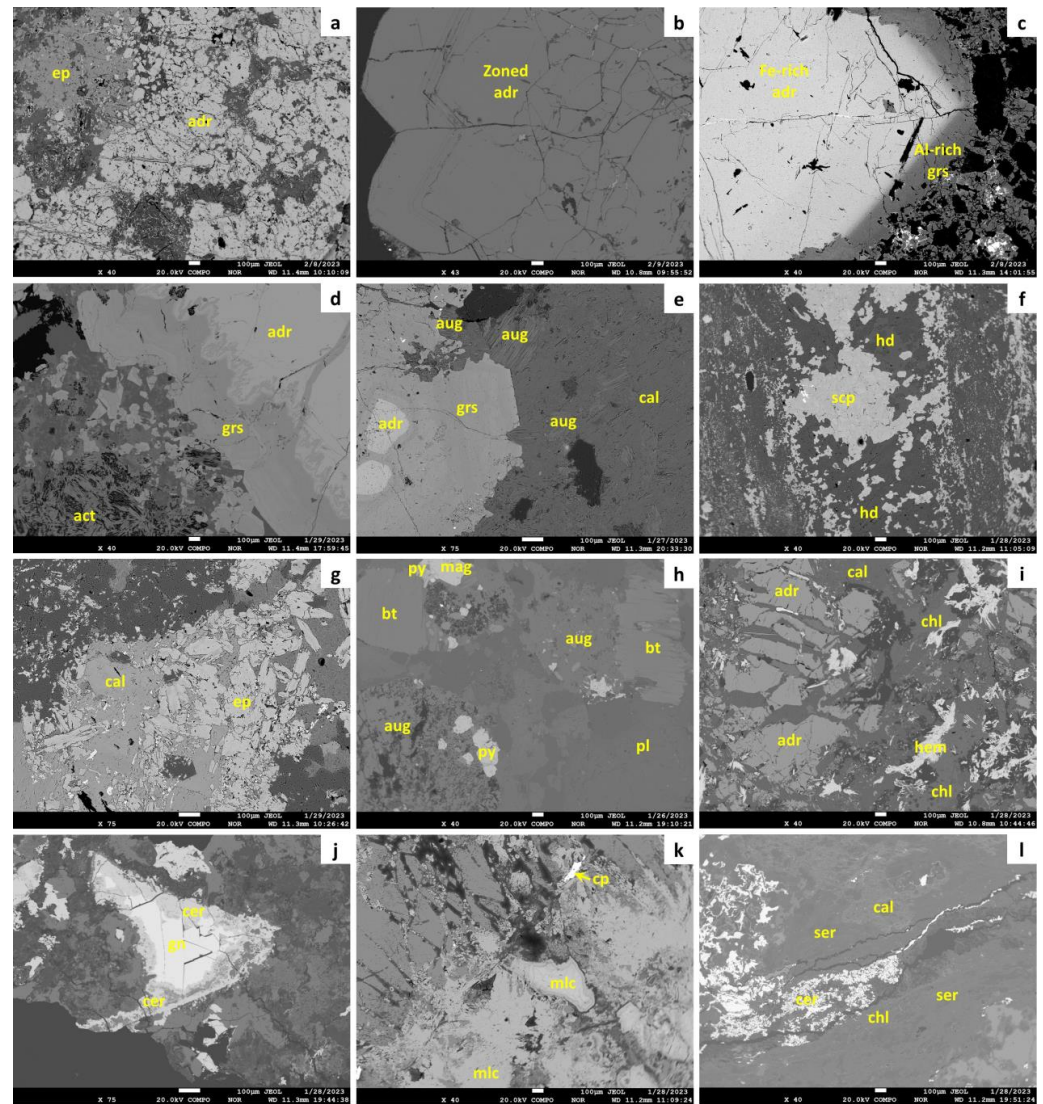


Figure 15. Backscattered electron images showing different minerals from various skarn zones. (a) Un-zoned andradite partially altered to epidote in the endoskarn zone. (b) Zoned andradite from the prograde proximal subzone. (c,d) Oscillatory zoning of the andradite (Fe-rich)–grossular (Al-rich) with actinolite in the retrograde subzone. (e) Augite associated with andradite–grossular and calcite in the endoskarn and proximal zones. (f) Hedenbergite associated with scapolite in the intermediate zone. (g) Epidote associated with calcite in the exoskarn proximal zone. (h) Biotite associated with augite, plagioclase, magnetite, and pyrite in the endoskarn zone. (i) Chlorite accompanied by andradite, calcite, pyrite, and specular hematite in the exoskarn proximal zones. (j) Cerussite pseudomorph after galena in the distal exoskarn zone. (k) Malachite pseudomorph after chalcopyrite in the distal exoskarn zone. (l) Sericite associated with calcite, chlorite, and cerussite in the distal zone. Abbreviations: actinolite (act), andradite (adr), augite (aug), biotite (bt), calcite (cal), cerussite (cer), chlorite (chl), chalcopyrite (cp), epidote (ep), galena (gn), grossular (grs), hedenbergite (hd), hematite (hem), magnetite (mag), malachite (mlc), plagioclase (pl), pyrite (py), scapolite (scp), sericite (ser).

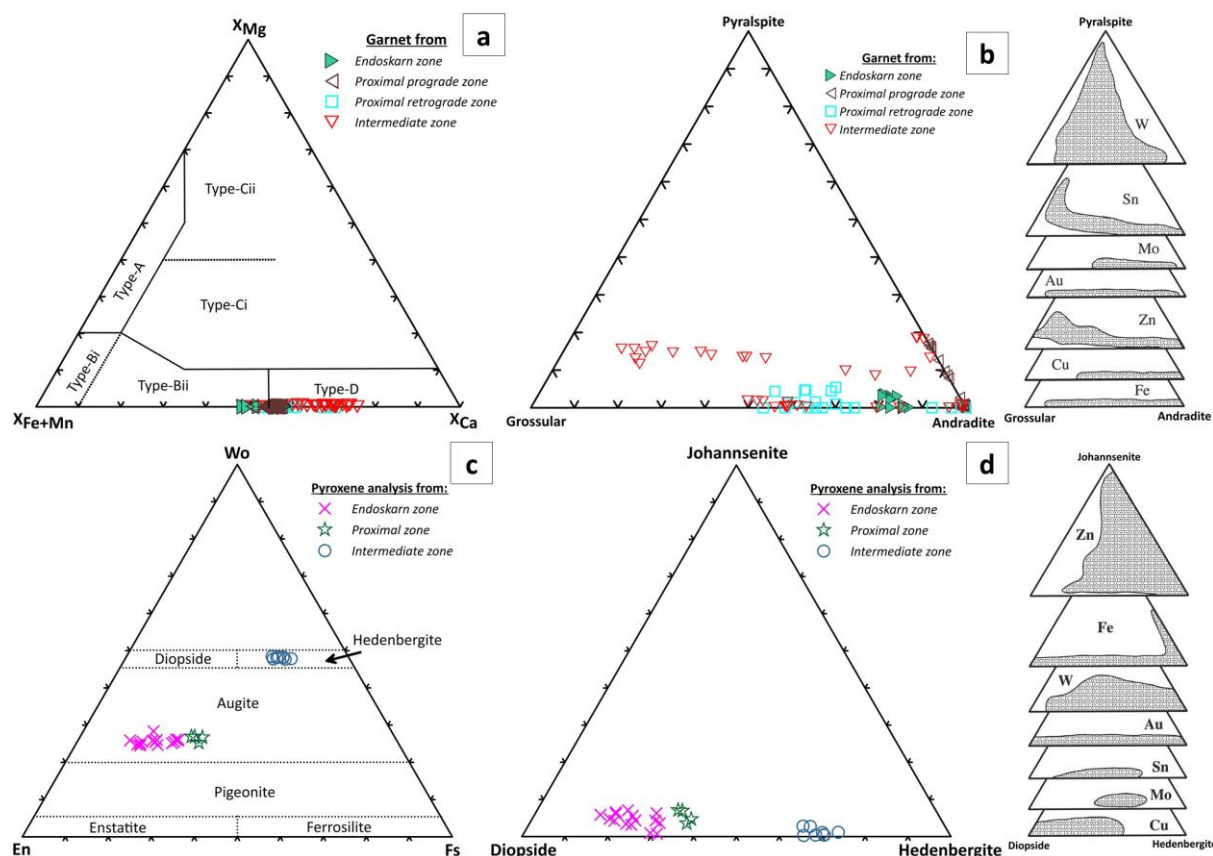


Figure 16. (a) Fe + Mn-Mg-Ca ternary diagram according to Mange and Morton [73], displaying definitions of garnet types A, Bi, Bii, Ci, Cii, and D. Most type A garnets are derived from high-grade granulite-facies metasediments or charnockites, with just a small amount originating from intermediate-acidic igneous rocks found deep in the crust. Granitoid (subtype Bi) and amphibolite-facies metasedimentary rocks (subtype Bii) are the sources of type B garnets. High-grade metabasites (subtype Ci) and pyroxenites and peridotites (subtype Cii) are the sources of type C garnets. Skarns, extremely low-grade metabasites, or calc-silicate granulites are the sources of type D garnets. (b) Ternary diagram showing compositional variation in garnet from the Yolindi Cu-Fe skarn deposit. The data for typical skarns worldwide are from Meinert, et al. [1]. (c) Plot of pyroxene composition in the Wo–En–Fs diagram according to Morimoto [74]. (d) Ternary diagram showing compositional variation in clinopyroxene from the Yolindi Cu-Fe skarn deposit. The data for typical skarns worldwide are from Meinert, et al. [1].

• Clinopyroxene

Clinopyroxene minerals, which show no compositional zoning, occur in the endoskarn and proximal zones as augite, along with andradite–grossular and calcite (Figure 15e), and in the intermediate zone as hedenbergite associated with scapolite (Figure 15f). The chemistry of the clinopyroxene minerals from the various skarn zones revealed that they are augite in composition, with a range of $En_{50.6-62.0}Fs_{12.1-23.2}Wo_{24.5-28.4}$ and $En_{44.8-47.2}Fs_{25.8-28.5}Wo_{25.2-26.9}$ and range of $Di_{65.5-78.7}Hd_{15.4-31.1}Jhn_{0.8-7.1}$ and $Di_{58.2-60.0}Hd_{32.8-37.1}Jhn_{3.6-7.1}$ for the endoskarn and proximal exoskarn zones, respectively, while they are hedenbergite with an average composition of $En_{16.0}Fs_{35.8}Wo_{48.2}$ and $Di_{30.5}Hd_{68.4}Jhn_{1.2}$ for the intermediate zone (Figure 16c and Table 4). The endoskarn zone augite has greater magnesium numbers ($\#Mg = 100 \times \#Mg / [\#Mg + \#Fe^{2+}]$), ranging from 68.5 to 83.7, than the proximal zone augite, which has a range of 61.1 to 64.6, whilst the intermediate zone hedenbergite has a low $\#Mg$ content with an average of 30.9 (Table 4). The low average TiO_2 , MnO , and Na_2O concentrations in clinopyroxene minerals from the endoskarn, proximal, and intermediate zones are 0.61, 1.87, and 0.75 wt.%; 0.03, 2.28, and 0.12 wt.%; and 0.01, 0.35, and 0.09 wt.%,

respectively (Table 4). These concentrations decrease from the endoskarn to the intermediate exoskarn zone. The classification diagram of pyroxene end-member compositions with diopside, johannsenite, and hedenbergite shows that the analyzed clinopyroxenes have higher diopside and hedenbergite contents and are mostly compatible with clinopyroxene from other worldwide Cu-Fe skarn deposits of Meinert, et al. [1] (Figure 16d).

- Scapolite

The scapolite mineral, which frequently occurs in Fe skarn deposits, forms in association with hedenbergite in the exoskarn intermediate zone (Figures 10c,d and 15f) due to the metasomatic interaction of highly abundant silicate fluids and carbonaceous host rocks that occurs. According to the EPMA data for the scapolite, its SiO₂, Al₂O₃, CaO, Na₂O, and Cl contents are higher, with ranges of 51.67–54.84 wt.%, 23.48–26.08 wt.%, 7.94–12.56 wt.%, 5.65–8.44 wt.%, and 2.68–3.53 wt.%, respectively, but its K₂O content is lower, with an average of 1.26 wt.% (Table 5). Furthermore, the % meionite (Me) of the analyzed scapolite ranges from 32.59 to 52.57, with an average of 42.96, indicating that this scapolite belongs to the late scapolite, which is a Cl-rich scapolite with averages of 33.3 and 2.96 wt.% for Me and Cl, respectively [75] (Table 5). Na_{2.04}K_{0.24}Ca_{1.69}Si_{7.71}Al_{14.29}Fe²⁺_{0.03}Ti_{0.001}O₂₄Cl_{10.75}F_{0.07} is the estimated formula for the studied scapolite (Table 5).

- Plagioclase

In the endoskarn zone, plagioclase occurred, along with andradite and augite. SiO₂ (58.0–65.4 wt.%), Al₂O₃ (21.2–26.1 wt.%), and Na₂O (6.6–8.1 wt.%) are all detected in significant concentrations, while CaO (3.2–7.7 wt.%) and K₂O (0.3–0.7 wt.%) are in relatively low amounts (Table 6). The triangle diagram of albite (Ab), anorthite (An), and orthoclase (Or) endmembers (Figure 17a) shows that the plagioclase is oligoclase and andesine. Considering this, the composition of plagioclase ranges from Ab_{59.4} to Ab_{79.7}, An_{18.0} to An_{37.5}, and Or_{1.6} to Or_{4.6}.

- Epidote

Epidote is an alteration mineral that has developed from the late replacement of garnet in the endoskarn and exoskarn proximal and intermediate zones associated with garnet, pyroxene, and calcite (Figures 6–11 and 15a,g). Table 7 shows that the content of each oxide in the representative EPMA data for the epidote from the endoskarn zone is in the following ranges: SiO₂: 31.9–33.4 wt.%, Al₂O₃: 23.0–26.2 wt.%, CaO: 20.5–21.6 wt.%, and FeO: 10.9–15.1 wt.%. According to Yavuz and Yıldırım [76], the stoichiometric element calculations based on 12.5 oxygens and the assumption of whole Fe as Fe³⁺ yielded total cation values for Si, Al + Fe + Ti, and Ca + Mn in the ranges of 2.7–2.8, 3.3–3.4, and 1.8–2.0, respectively, for endoskarn epidote. In contrast, the proximal epidote contains SiO₂ (15.5–32.7 wt.%), Al₂O₃ (13.4–26.1 wt.%), CaO (16.2–21.2 wt.%), and FeO (10.5–14.5 wt.%), with the values of total cations for Si, Al + Fe + Ti, and Ca + Mn, respectively, falling within the ranges of 2.2–2.8, 3.37–3.43, and 1.8–2.4. The Fe/(Fe + Al) ratios for the epidote from the endoskarn and proximal zones, respectively, are between 0.23 and 0.32 and between 0.24 and 0.36, suggesting that they originated from the replacement of grossular-rich garnet and were classified as clinozoisite (Figure 17b).

- Biotite

Eighteen EPMA spots of representative biotite were chosen from endoskarn zone samples associated with augite, plagioclase, magnetite, and pyrite (Figure 15h) and recalculated to yield their formulas (Table 8). The average X_{Mg} = Mg/(Mg + Fe) and X_{Fe} = Fe/(Fe + Mg) values of biotite are 0.65 and 0.35, respectively, indicating that this biotite is classed as Mg-biotite according to Tischendorf, et al. [77] [(Mg-Li) vs. (Fe^{tot} + Mn + Ti-Al^{VI})] diagram (Figure 17c). Nachit, et al. [78] distinguished three kinds of biotite using the (FeO + MnO)-MgO-TiO₂ ternary diagram (Figure 17d): primary magmatic biotite, re-equilibrated biotite, and newly formed biotite. The analyzed biotites are categorized as primary magmatic biotite [79] (Figure 17d). Because the Ti concentrations (apfu) of the studied biotite range from 0.47 to 0.54, they fit within the geothermometer calibration range (0.04–0.60)

of Henry, et al. [80]. The Ti-in-biotite geothermometer application is, thus, appropriate for predicting the equilibration temperature of biotite by calculating temperatures directly from this equation: According to Henry et al. (2005), $T (^{\circ}\text{C}) = ([\ln(\text{Ti}) - a - c(X_{\text{Mg}})^3]/b)_{0.333}$, where Ti is the number of atoms per formula unit (apfu) normalized on the basis of 22 O atoms, $a = -2.3594$, $b = 4.648210^{-9}$, and $c = -1.7283$. This equation predicts a temperature range of 436 $^{\circ}\text{C}$ to 480 $^{\circ}\text{C}$ for the studied magmatic biotite from the endoskarn zone, with an average of 463 $^{\circ}\text{C}$ (Table 8) generated within the calc-alkaline orogenic suites (Figure 17e) from the crust–mantle source (Figure 17f).

Table 7. Representative electron microprobe data of epidote from the endoskarn and proximal zones of the Yolindi Cu-Fe skarn deposit.

Dataset	Endoskarn/Epidote ($n = 7$)			Proximal/Epidote ($n = 7$)		
	Min.	Max.	Av.	Min.	Max.	Av.
SiO ₂	31.9	33.4	32.7	15.5	32.7	29.9
TiO ₂	0.0	0.1	0.0	0.0	0.3	0.1
Al ₂ O ₃	23.0	26.2	24.2	13.4	26.1	23.1
FeO	10.9	15.1	13.4	10.5	14.5	12.8
CaO	20.5	21.6	21.1	16.2	21.2	20.0
F	0.0	0.2	0.0	0.0	0.2	0.0
O = F	0.0	0.1	0.0	0.0	0.1	0.0
Total	91.1	91.8	91.5	55.8	91.7	85.9
<i>Calculated cations based on 12.5 oxygen</i>						
Si	2.7	2.8	2.7	2.2	2.8	2.7
Al	2.3	2.6	2.4	2.2	2.6	2.4
Fe ³⁺	0.8	1.1	0.9	0.8	1.2	1.0
Ca	1.8	2.0	1.9	1.8	2.4	1.9
Total	8.0	8.0	8.0	8.0	8.0	8.0
<i>Epidote subgroup</i>	<i>Clinozoisite</i>			<i>Clinozoisite</i>		
Fe/Fe + Al	0.2	0.3	0.3	0.2	0.4	0.3
Al + Fe + Ti	3.3	3.4	3.3	3.4	3.4	3.4
Ca + Mn	1.8	2.0	1.9	1.8	2.4	1.9

Table 8. Representative electron microprobe data of biotite from endoskarn zone of the Yolindi Cu-Fe skarn deposit.

Dataset	Endoskarn/Biotite ($n = 18$)		
	Min.	Max.	Av.
SiO ₂	37.0	38.1	37.4
TiO ₂	4.2	4.9	4.6
Al ₂ O ₃	12.9	13.8	13.4
FeO	13.2	15.6	14.2
MnO	0.0	0.0	0.0
MgO	13.6	15.3	14.6
Na ₂ O	0.1	0.3	0.2
K ₂ O	9.7	10.1	9.8
H ₂ O*	3.6	3.8	3.7
Li ₂ O*	1.1	1.4	1.2
F	0.3	0.8	0.6
Cl	0.3	0.4	0.4
<i>Atoms per formula unit (apfu)</i>			
Si	5.5	5.6	5.6
Al ^{IV}	2.3	2.4	2.3
Al ^{VI}	0.0	0.0	0.0
Ti	0.5	0.5	0.5
Fe	1.6	1.9	1.8
Mn	0.0	0.0	0.0

Table 8. Cont.

Dataset	Endoskarn/Biotite (<i>n</i> = 18)		
	Min.	Max.	Av.
Mg	3.0	3.4	3.2
Na	0.0	0.1	0.1
K	1.8	1.9	1.9
OH*	3.5	3.8	3.6
F	0.1	0.4	0.3
Cl	0.1	0.1	0.1
Li*	0.7	0.8	0.7
Total	20.0	20.1	20.1
<i>Parameters</i>			
Al total	2.3	2.4	2.3
Mg-Li	2.2	2.7	2.5
Fe + Mn + Ti-Al ^{VI}	2.1	2.5	2.3
X _(Mg) = Mg/(Mg + Fe)	0.6	0.7	0.6
X _(Fe) = Fe/Fe + Mg	0.3	0.4	0.4
FeO/(FeO + MgO)	0.5	0.5	0.5
FeO + MnO	13.2	15.6	14.2
ln(Ti)	−0.7	−0.6	−0.7
T (°C)	436.2	479.9	462.5

Li₂O* and H₂O* calculations after Tindle and Webb [81].

• Chlorite

In the exoskarn zones, chlorite forms as olive-green flakes accompanied by andradite, calcite, pyrite, and specular hematite (Figures 10 and 15i). EPMA data for chlorite flakes were recalculated using a formula unit (apfu) of 28 oxygen atoms (Table 9). The proximal zone had greater Mg concentrations than the intermediate and distal zones, with values ranging from 2.6–5.4 apfu, 1.1–2.8 apfu, and 0.9–1.5 apfu, respectively, decreasing from proximal to distal zones (Table 9). The total Fe contents, on the other hand, rise from proximal to distal zones, with values ranging from 3.3–14.9 apfu, 14.8–19.9 apfu, and 19.8–21.1 apfu for the proximal, intermediate, and distal zones, respectively (Table 9). As a result, they are primarily categorized as Fe-chlorite (chamosite) based on the (Al^{IV})-Mg-Fe ternary diagram of Zane and Weiss [82], with the exception of a few proximal chlorite spots that are classified as Mg-chlorite (clinocllore) (Figure 17g). When the estimated formation temperatures for these chlorite types were calculated using the empirical Si-Al^{IV} substitution geothermometer of Cathelineau [83] (Table 9), they showed a decrease from proximal (T = an average of 286 °C) to distal (T = an average of 152 °C) throughout the intermediate zone (T = an average of 179 °C).

Table 9. Representative electron microprobe data of chlorite from different skarn zones of the Yolindi Cu-Fe skarn deposit.

Dataset	Proximal/Chlorite (<i>n</i> = 17)			Intermediate/Chlorite (<i>n</i> = 8)			Distal/Chlorite (<i>n</i> = 8)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
SiO ₂	22.0	31.6	25.8	27.0	27.8	27.4	24.4	27.9	26.2
TiO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Al ₂ O ₃	11.5	20.0	17.9	17.2	19.1	18.2	17.8	22.6	20.0
FeO	16.4	30.7	27.1	23.4	34.5	29.7	10.9	16.8	13.6
MnO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MgO	9.2	16.4	12.7	9.0	15.4	11.8	8.2	13.8	10.9
CaO	0.1	0.4	0.2	0.0	0.2	0.1	0.1	0.2	0.1
Na ₂ O	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.0	0.2	0.1	0.0	0.3	0.1	0.0	0.1	0.1

Table 9. Cont.

Dataset	Proximal/Chlorite (<i>n</i> = 17)			Intermediate/Chlorite (<i>n</i> = 8)			Distal/Chlorite (<i>n</i> = 8)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
Cr ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F	0.0	0.1	0.0	0.0	0.2	0.1	0.0	0.3	0.1
Cl	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	59.1	99.6	83.8	76.8	97.7	87.3	61.5	81.7	71.0
<i>Atoms per formula unit (apfu)</i>									
Si	3.0	7.1	5.3	2.2	3.3	2.7	1.6	2.2	1.9
Al ^{IV}	0.9	3.3	2.1	0.7	1.2	0.9	0.6	0.7	0.6
Al ^{VI}	0.0	2.9	1.8	0.0	0.0	0.0	0.0	0.0	0.0
Fe ³⁺	0.0	0.8	0.2	0.0	0.0	0.0	0.0	0.0	0.0
Fe ²⁺	2.5	14.9	6.7	14.8	19.9	17.7	19.8	21.1	20.5
Mn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mg	2.6	5.4	3.9	1.1	2.8	1.8	0.9	1.5	1.2
K	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0
OH*	15.3	16.0	15.9	15.9	16.0	16.0	15.9	16.0	15.9
F	0.0	0.2	0.1	0.0	0.1	0.0	0.0	0.1	0.1
Cl	0.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	35.0	38.0	36.1	38.1	39.9	39.1	39.7	40.5	40.2
<i>Parameters</i>									
Fe/Fe + Mg	0.4	0.9	0.6	0.8	0.9	0.9	0.9	1.0	0.9
Al total	1.4	5.2	3.9	0.7	1.2	0.9	0.6	0.7	0.6
Fe/Fe + Mg	0.4	0.9	0.6	0.8	0.9	0.9	0.9	1.0	0.9
FeO calc	12.7	30.7	24.9	23.4	34.5	29.7	10.9	16.8	13.6
Fe ₂ O ₃ calc	0.0	4.5	1.4	0.0	0.0	0.0	0.0	0.0	0.0
Al iv c (corrected)	1.2	3.7	2.5	1.4	1.8	1.5	1.2	1.3	1.3
Fe = Fe ²⁺ + Fe ³⁺	3.3	14.9	6.9	14.8	19.9	17.7	19.8	21.1	20.5
Fe + Mg	8.2	17.5	10.8	17.6	21.0	19.5	20.8	22.3	21.7
T (°C)	143.2	414.9	285.7	161.8	205.3	179.3	146.4	158.6	151.6

Reformatted oxide percentages based on 28 oxygens (with Fe²⁺/Fe³⁺ and OH calculated assuming full site occupancy) after Tindle [84].

- Amphibole

Table 10 shows the chemical compositions of amphibole from several skarn zones in the Yolindi region (e.g., endoskarn, proximal, and intermediate zones). This amphibole is frequently associated with andradite–grossular, and calcite formed by the pseudomorphic replacement of pyroxene (Figure 15d). The analyzed amphiboles are magnesian, displaying actinolite-rich compositions (Figure 17h) with a narrow range of Si content having 7.53–8.05 apfu, 7.90–8.17 apfu, and 8.10–8.19 apfu; and a Mg/(Mg + Fe²⁺) ratio with a range of 0.69–0.77, 0.55–0.67, and 0.64–0.68 for amphibole from endoskarn, proximal, and intermediate zones, respectively (Table 10).

- Carbonate

Calcite was detected in the proximal (Figure 8) and intermediate exoskarn zones along with andradite–grossular, augite, and epidote (Figures 10 and 15e,g), and cerussite and malachite were detected in the distal exoskarn zone pseudomorph after galena and chalcopyrite, respectively (Figures 10 and 15j,k). The EMPA data show that the calcite mineral has higher amounts of CaCO₃ with ranges of 97.12–99.86 and 99.16–99.66 for the proximal and intermediate zones, respectively (Table 11), and very low amounts of FeCO₃ with ranges of 0.13–2.86 and 0.33–0.77 for the proximal and intermediate zones, respectively (Figure 17f).

Table 10. Representative electron microprobe data of amphibole from the different skarn zones of the Yolindi Cu-Fe skarn deposit.

Dataset	Endoskarn/Amphibole (<i>n</i> = 5)			Proximal/Amphibole (<i>n</i> = 11)			Intermediate/Amphibole (<i>n</i> = 4)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
SiO ₂	53.07	57.55	55.12	44.74	54.06	50.38	54.97	55.57	55.23
TiO ₂	0.12	1.08	0.58	0.00	0.03	0.01	0.00	0.03	0.01
Al ₂ O ₃	1.47	4.88	3.39	0.28	1.44	0.79	0.84	1.20	0.95
FeO	9.29	12.19	10.62	10.76	17.52	14.75	13.31	13.82	13.60
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	15.09	17.74	16.34	11.20	18.31	14.02	13.97	15.72	15.02
CaO	9.25	11.18	10.44	0.23	19.45	8.18	7.91	10.11	9.04
Na ₂ O	0.45	1.31	0.85	0.02	0.23	0.12	0.16	0.22	0.19
K ₂ O	0.10	1.37	0.49	0.02	0.20	0.07	0.07	0.11	0.09
<i>Atom</i>									
Si	7.53	8.05	7.79	7.90	8.17	8.03	8.10	8.19	8.15
Ti	0.01	0.12	0.06	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.24	0.82	0.57	0.05	0.27	0.15	0.15	0.21	0.17
Fe ²⁺	1.08	1.45	1.26	1.34	2.37	1.98	1.64	1.72	1.68
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	3.19	3.69	3.44	2.48	4.68	3.36	3.09	3.46	3.30
Ca	1.41	1.69	1.58	0.04	3.10	1.35	1.25	1.61	1.43
Na	0.12	0.36	0.23	0.01	0.07	0.04	0.05	0.06	0.05
K	0.02	0.25	0.09	0.00	0.04	0.01	0.01	0.02	0.02
H	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Mg/(Mg + Fe ²⁺)	0.69	0.77	0.73	0.55	0.67	0.63	0.64	0.68	0.66

Table 11. Representative electron microprobe data of calcite and cerussite from the different skarn zones of the Yolindi Cu-Fe skarn deposit.

Dataset	Proximal/Calcite (<i>n</i> = 22)			Intermediate/Calcite (<i>n</i> = 4)			Distal/Cerussite (<i>n</i> = 17)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
<i>Wt% element</i>									
Ca	21.10	23.85	22.58	22.82	23.41	23.10	0.00	0.08	0.03
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00
Fe	0.04	0.94	0.23	0.11	0.25	0.20	0.00	0.16	0.03
Sr	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.02	0.00
Pb	0.00	0.02	0.00	0.00	0.01	0.00	35.91	71.50	68.53
C backcalc	6.34	7.23	6.82	6.90	7.06	6.97	2.10	4.15	3.99
O backcalc	25.35	28.89	27.24	27.56	28.21	27.84	8.38	16.59	15.95
Total	52.88	60.37	56.88	57.56	58.89	58.12	46.46	92.24	88.54
<i>Atomic fraction</i>									
Ca	0.53	0.60	0.56	0.57	0.58	0.58	0.00	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.35	0.33
C	0.53	0.60	0.57	0.57	0.59	0.58	0.17	0.35	0.33
O	1.58	1.81	1.70	1.72	1.76	1.74	0.52	1.04	1.00
<i>Structural formulae basis on cation per 2 oxygens</i>									
Ca	1.94	2.00	1.99	1.98	1.99	1.99	0.00	0.01	0.01
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.06	0.01	0.01	0.02	0.01	0.00	0.02	0.00

Table 11. Cont.

Dataset	Proximal/Calcite (n = 22)			Intermediate/Calcite (n = 4)			Distal/Cerussite (n = 17)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	0.00	0.00	0.00	0.00	0.00	0.00	1.98	2.00	1.99
C	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
O	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
% Molecule									
CaCO ₃	97.12	99.86	99.25	99.16	99.66	99.37	0.01	0.61	0.27
MgCO ₃	0.00	0.02	0.01	0.00	0.01	0.00	0.00	0.03	0.01
MnCO ₃	0.00	0.03	0.01	0.00	0.03	0.01	0.00	0.05	0.01
FeCO ₃	0.13	2.86	0.72	0.33	0.77	0.61	0.00	0.85	0.17
SrCO ₃	0.00	0.02	0.01	0.00	0.02	0.01	0.00	0.10	0.02
PbCO ₃	0.00	0.02	0.00	0.00	0.01	0.00	98.85	99.97	99.53
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
FeCO ₃ + MnCO ₃	0.13	2.87	0.73	0.33	0.81	0.61			

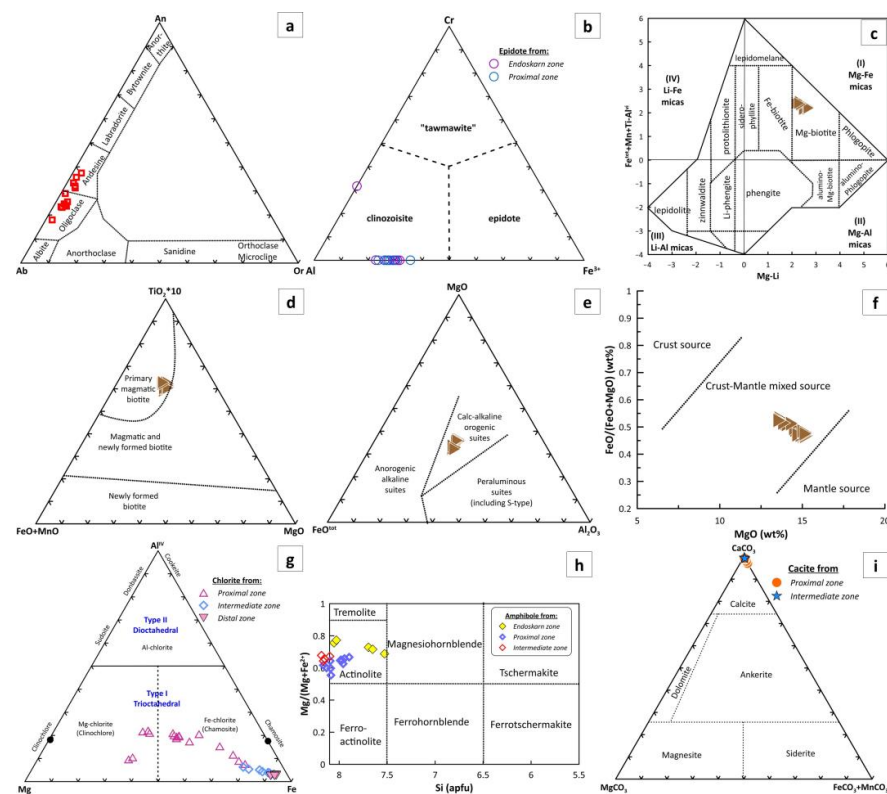


Figure 17. (a) An-Ab-Or ternary diagram according to Deer, et al. [75] showing the composition of the plagioclase from the endoskarn zone. (b) Ternary diagram Cr^{3+} -Al- Fe^{3+} showing the nomenclature of monoclinic epidote-supergrupp minerals belonging to the clinozoisite subgroup according to Franz and Liebscher [85]. (c) Classification of biotite on the (Mg-Li) vs. ($\text{Fe}^{\text{tot}} + \text{Mn} + \text{Ti}-\text{Al}^{\text{VI}}$) diagram according to Tischendorf, et al. [77]. (d) (FeO + MnO)-MgO-TiO₂ ternary diagram of biotite according to Nachit, et al. [78], Nachit, et al. [86]. (e) MgO-FeO^{tot}-Al₂O₃ discriminating diagrams for biotite according to Abdel-rahman [87]. (f) FeO/(FeO + MgO) vs. MgO (wt.%) binary diagram according to Zhou [88]. (g) (Al^{IV})-Mg-Fe chlorite classification diagram according to Zane and Weiss [82]. (h) Classification of the calcic amphiboles according to Leake, et al. [89]. (i) CaCO₃-MgCO₃-FeCO₃ + MnCO₃ ternary diagram of carbonate minerals [75].

- Sericite

Sericite is a very fine-grained white mica of a white and yellowish tint that is generally formed by the breakdown of feldspars in the distal zone associated with calcite, chlorite, cerussite, and malachite (Figures 10g–l and 15l). The sericite electron microprobe results (Table 12) revealed that the muscovite content was abundant in all the investigated flakes (average $X_{Ms} = 0.99$) and that the phengite content ($Mg + Fe_{apfu}$) ranged from 0.55 to 0.86.

Table 12. Representative electron microprobe data of sericite from the distal exoskarn zone of the Yolindi Cu-Fe skarn deposit.

Dataset	Distal/Sericite ($n = 3$)		
	Min.	Max.	Av.
SiO ₂	38.30	41.57	40.20
TiO ₂	0.02	0.05	0.03
Al ₂ O ₃	25.70	28.87	27.70
FeO	1.62	3.19	2.19
MgO	1.41	1.88	1.72
CaO	0.12	0.28	0.21
Na ₂ O	0.00	0.05	0.03
K ₂ O	7.23	8.87	8.10
Cl	0.01	0.03	0.02
F	0.20	0.36	0.30
TOTAL	76.29	82.49	79.85
O = F,Cl	0.09	0.15	0.13
TOTAL	76.15	82.34	79.72
No Anions	22.00	24.00	23.00
<i>Formula</i>			
Si	5.86	6.36	6.15
Ti	0.00	0.01	0.00
Al ^{IV}	1.64	2.14	1.85
Al ^{VI}	2.50	3.51	3.15
Al ^{Total}	4.64	5.21	5.00
Fe(ii)	0.21	0.41	0.28
Mg	0.32	0.43	0.39
Ca	0.02	0.05	0.03
Na	0.00	0.02	0.01
K	1.41	1.73	1.58
Cl	0.00	0.01	0.01
F	0.11	0.18	0.15
Total	12.79	13.93	13.45
Fe/(Fe + Mg)	0.33	0.49	0.41
X_{Ms}	0.99	1.00	1.00
Fe + Mg	0.55	0.84	0.67
Si + Mg + Fe	6.70	7.00	6.82

- Ore mineral chemistry
- Magnetite

In association with andradite, augite, hedenbergite, calcite, pyrite, and chalcopryrite, the magnetite minerals formed in the endoskarn and exoskarn proximal and intermediate zones and were partially martitized to hematite (Figures 6–9 and 18a). Table 13 shows the EPMA results for endoskarn, proximal, and intermediate magnetite, with FeO content of 92.66–95.48 wt.% (average 94.53 wt.%), 90.07–96.72 (average 93.77 wt.%), and 91.92–93.84 wt.% (average 92.99 wt.%), respectively. From the endoskarn to the intermediate zone, the SiO₂ and Al₂O₃ contents of the analyzed magnetite increased on average by 0.17, 0.48, and 0.55 wt.% and 0.07, 0.09, and 0.11 wt.% for the endoskarn, proximal, and intermediate zones, respectively (Table 13). Low amounts of TiO₂, MnO, MgO, and CaO were found with average concentrations of 0.06, 0.01, and 0.01 wt.%; 0.04, 0.16, and

0.08 wt.%; 0.03, 0.05, and 0.05 wt.%; and 0.03, 0.03, and 0.06 wt.% for endoskarn, proximal, and intermediate zones, respectively. Lin [90] presented a $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-(MgO + MnO)}$ ternary diagram to differentiate magnetite from different deposit types or metallogenic settings. The endoskarn magnetite has magmatic affinity, falling primarily in the fields of magmatic and accessory mineral types (Figure 18b), whereas the proximal and intermediate magnetites have principal hydrothermal affinity, plotting mostly in the fields of skarn and contact metasomatic types. This is also evident in the $(\text{Ca} + \text{Al} + \text{Mn})$ vs. $(\text{Ti} + \text{V})$ magnetite discrimination diagram [91], where the proximal and intermediate magnetite fall into the skarn field (Figure 18c), implying a hydrothermal metasomatic origin, whereas the endoskarn magnetite has a different origin than skarn.

Table 13. Representative electron microprobe data of magnetite from the different skarn zones of the Yolindi Cu-Fe skarn deposit.

Dataset	Endoskarn/Magnetite (n = 5)			Proximal/Magnetite (n = 14)			Intermediate/Magnetite (n = 6)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
SiO ₂	0.00	0.57	0.17	0.03	1.30	0.48	0.29	0.83	0.55
TiO ₂	0.02	0.11	0.06	0.00	0.05	0.01	0.00	0.02	0.01
Al ₂ O ₃	0.02	0.14	0.07	0.00	0.23	0.09	0.04	0.18	0.11
Cr ₂ O ₃	0.00	0.01	0.01	0.00	0.03	0.01	0.00	0.02	0.00
V ₂ O ₃	0.01	0.26	0.08	0.00	0.05	0.01	0.00	0.01	0.00
FeO	92.66	95.48	94.53	90.07	96.72	93.77	91.92	93.84	92.99
MnO	0.02	0.10	0.04	0.08	0.25	0.16	0.05	0.16	0.08
MgO	0.01	0.06	0.03	0.00	0.28	0.05	0.01	0.10	0.05
CaO	0.00	0.11	0.03	0.01	0.09	0.03	0.02	0.11	0.06
ZnO	0.00	0.04	0.01	0.00	0.03	0.01	0.00	0.01	0.01
Total	92.74	96.88	95.03	90.19	99.02	94.61	92.32	95.26	93.85
No Oxyg Atoms	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00	32.00
Si	0.00	0.17	0.05	0.01	0.39	0.15	0.09	0.25	0.17
Ti	0.00	0.03	0.01	0.00	0.01	0.00	0.00	0.00	0.00
Al	0.01	0.05	0.02	0.00	0.08	0.03	0.01	0.06	0.04
Cr	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
V	0.00	0.06	0.02	0.00	0.01	0.00	0.00	0.00	0.00
Fe(iii)	15.49	15.97	15.82	15.15	15.98	15.67	15.43	15.81	15.62
Fe(ii)	7.98	8.12	8.03	7.97	8.30	8.08	8.06	8.15	8.11
Mn	0.00	0.02	0.01	0.02	0.06	0.04	0.01	0.04	0.02
Mg	0.00	0.03	0.01	0.00	0.13	0.02	0.00	0.04	0.02
Ca	0.00	0.04	0.01	0.00	0.03	0.01	0.01	0.04	0.02
Zn	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Total	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00
Parameter									
MgO + MnO	0.03	0.10	0.06	0.10	0.52	0.21	0.06	0.23	0.13
Ti + V wt%	0.02	0.21	0.08	0.00	0.05	0.01	0.00	0.01	0.00
Ca + Al + Mn wt%	0.03	0.16	0.08	0.08	0.24	0.17	0.08	0.22	0.15

- Chalcopyrite

Chalcopyrite is the most prevalent base metal sulfide (BMS) in the Yolindi area, where it is mostly associated with specular hematite, pyrite, and magnetite (Figures 8, 10, and 18d). Its EPMA results show that the Cu concentrations vary from 28.68 to 29.42 wt.%, while the Fe and S contents range from 27.38 to 28.06 weight percent and from 41.76 to 42.71 wt.%, respectively, with the derived structural formula $\text{Cu}_{0.81}\text{Fe}_{0.87}\text{Mo}_{0.01}\text{S}_{2.30}$ (average), which is near the stoichiometric chalcopyrite (Table 14). Molybdenum (Mo) levels in chalcopyrite range from 0.63 to 0.69 wt.%.

- Pyrite

Pyrite is the most common Fe-sulfide found in endoskarn and exoskarn zones associated with magnetite, chalcopyrite, specular hematite, andradite, and calcite (Figures 6, 8, 10, and 18d–e), with Fe and S contents ranging from 41.25 to 43.64 wt.% and 53.04 to 56.90 wt.%, respectively (Table 14). Pyrite contains trace amounts of Mo and Ni, with an average of 0.97 wt.% and 0.25 wt.%, respectively. As a result, the estimated pyrite structural formula is $\text{Fe}_{0.91}\text{Ni}_{0.01}\text{Mo}_{0.01}\text{S}_{2.07}$ (average), which is virtually identical to the stoichiometric pyrite.

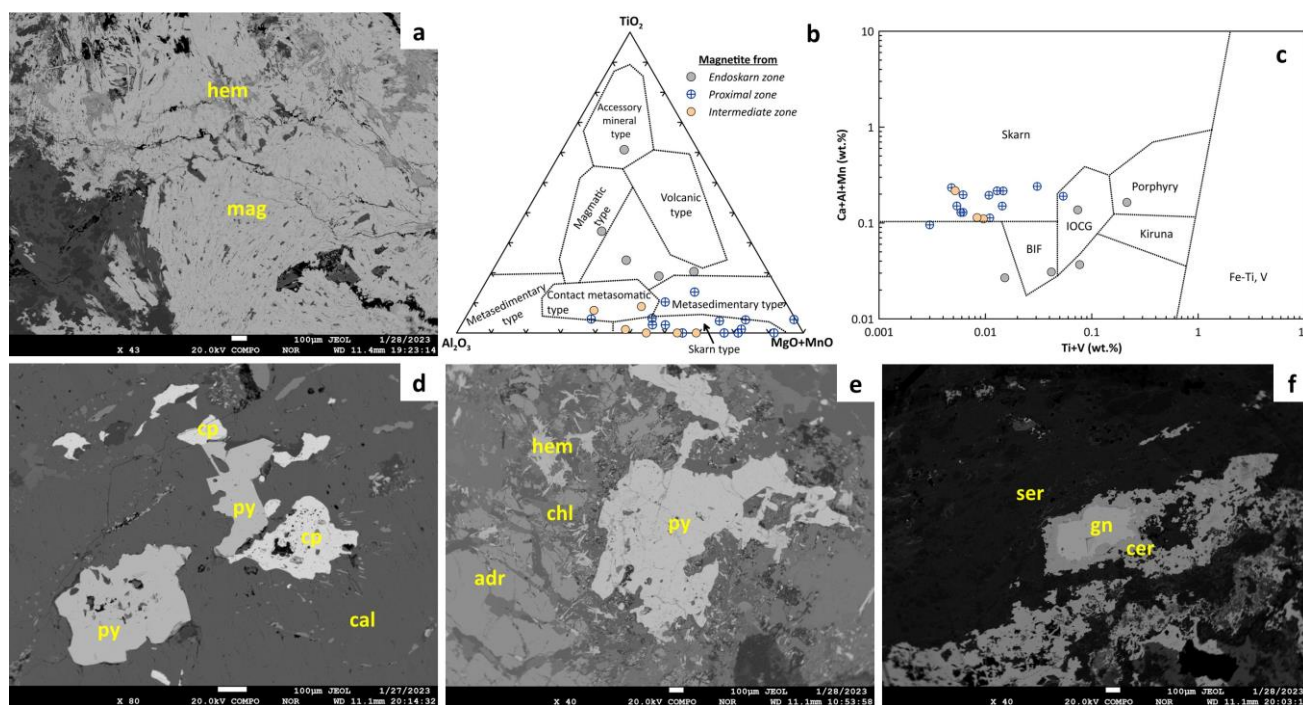


Figure 18. (a) Backscattered electron images of the magnetite in association with hematite in the proximal zone. (b) $\text{TiO}_2\text{--Al}_2\text{O}_3\text{--(MgO + MnO)}$ ternary diagram of the analyzed magnetite according to Lin [90]. (c) $(\text{Ca} + \text{Al} + \text{Mn})$ vs. $(\text{Ti} + \text{V})$ magnetite discrimination diagram [91]. (d) Backscattered image of the chalcopyrite associated with pyrite in the intermediate zones. (e) Backscattered image of the pyrite with specular hematite, andradite, chlorite in the intermediate zone. (f) Backscattered image of the galena that mostly altered to cerussite associated with sericite in the distal zone. Abbreviations: andradite (adr), calcite (cal), cerussite (cer), chlorite (chl), chalcopyrite (cp), galena (gn), hematite (hem), magnetite (mag), pyrite (py), sericite (ser).

- Galena

Galena was encountered in the distal exoskarn with sericite, chalcopyrite, and malachite, and it was mostly altered to cerussite (Figures 10, 15j,l, and 18f). The EPMA data show that it includes 88.07 wt.% Pb and 10.93 wt.% S on average, with less amounts of Co and Ni, averaging 0.13 and 0.16 wt.%, respectively (Table 14). Consequently, the calculated structural formula is $\text{Pb}_{1.10}\text{Co}_{0.01}\text{Ni}_{0.01}\text{S}_{0.88}$.

- Cerussite

Cerussite is a secondary lead carbonate mineral that forms in the oxidized zone of the distal exoskarn zone. It is a common alteration product of galena (Figures 10j,k, 15j,l, and 18f) during the retrograde stage, when the cooling of the system and ingress of external fluids, particularly meteoric waters, lead to the oxidation of primary sulfides. The EPMA data show that the cerussite has a higher PbCO_3 amount with a range of 98.85 and 99.97 and low amounts of CaCO_3 , FeCO_3 , and SrCO_3 , with an average of 0.27, 0.17, and 0.02 (Table 11).

Table 14. Representative electron microprobe data of sulfide minerals from the different skarn zones of the Yolindi Cu-Fe skarn deposit.

Dataset	Chalcopyrite (<i>n</i> = 4)			Pyrite (<i>n</i> = 40)			Galena (<i>n</i> = 7)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
S	41.76	42.71	42.09	53.04	56.90	55.15	10.24	11.48	10.93
Fe	27.38	28.06	27.61	41.25	43.64	42.48	0.00	0.02	0.01
Te	0.00	0.01	0.00	0.00	0.02	0.00	0.01	0.04	0.02
Cu	28.68	29.42	29.18	0.00	0.14	0.04	0.00	0.04	0.01
Au	0.00	0.01	0.00	0.00	0.04	0.01	0.00	0.02	0.00
As	0.00	0.05	0.03	0.00	0.60	0.12	0.00	0.04	0.01
Co	0.00	0.22	0.14	0.00	0.33	0.04	0.00	0.23	0.13
Ni	0.00	0.22	0.11	0.00	1.08	0.25	0.00	0.51	0.16
Ag	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.04	0.02
Sb	0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.02	0.01
Zn	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.02	0.00
Sn							0.00	0.01	0.00
Pb	0.00	0.00	0.00	0.00	0.00	0.00	87.29	88.75	88.07
Cr							0.00	0.01	0.00
Hg	0.00	0.00	0.00	0.00	0.05	0.02	0.00	0.03	0.00
Mo	0.63	0.69	0.66	0.91	1.05	0.97	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00
Bi	0.00	0.05	0.01	0.00	0.04	0.00	0.00	0.00	0.00
Total	99.67	100.02	99.86	97.42	100.39	99.19	99.02	99.75	99.49
atom%									
S	57.21	58.24	57.62	67.59	70.17	68.84	42.34	45.66	44.13
Fe	21.44	22.07	21.70	29.36	31.51	30.45	0.00	0.05	0.03
Te	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.04	0.02
Cu	19.73	20.35	20.16	0.00	0.09	0.03	0.00	0.08	0.02
Au	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00
As	0.00	0.03	0.02	0.00	0.32	0.06	0.00	0.06	0.01
Co	0.00	0.16	0.11	0.00	0.22	0.03	0.00	0.49	0.28
Ni	0.00	0.16	0.09	0.00	0.74	0.17	0.00	1.13	0.36
Ag	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.04	0.02
Sb	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.03	0.01
Zn	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.04	0.01
Sn	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00
Pb	0.00	0.00	0.00	0.00	0.00	0.00	53.71	57.00	55.09
Cr	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.03	0.01
Hg	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.00
Mo	0.29	0.31	0.30	0.38	0.44	0.41	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Bi	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Formula	$Cu_{0.81}Fe_{0.87}Mo_{0.01}S_{2.30}$			$Fe_{0.91}Ni_{0.01}Mo_{0.01}S_{2.07}$			$Pb_{1.10}Co_{0.01}Ni_{0.01}S_{0.88}$		
S	2.29	2.33	2.30	2.03	2.10	2.07	0.85	0.91	0.88
Fe	0.86	0.88	0.87	0.88	0.95	0.91			
Cu	0.79	0.81	0.81						
As									
Co							0.00	0.01	0.01
Ni				0.00	0.02	0.01	0.00	0.02	0.01
Pb							1.07	1.14	1.10
Mo	0.01	0.01	0.01	0.01	0.01	0.01			
Sum	4.00	4.00	4.00	3.00	3.00	3.00	2.00	2.00	2.00

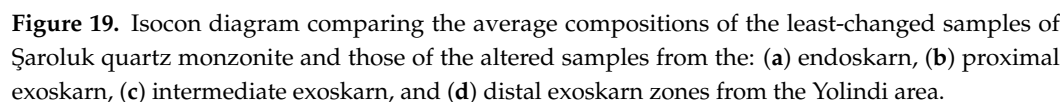
6. Discussion

6.1. Impact of the Alterations

In skarn deposits, mass balance calculations assist to quantify elemental gains, losses, and redistributions during the transformation from unaltered rock to skarn. Depending on the fluid composition, temperature, pH, Eh, and host-rock compositions, the chemical

ion exchange between host/wall rocks and hydrothermal fluid results in the formation of new altered minerals and alteration zones [32,92,93]. The gain and loss of rock mass components is common during hydrothermal alteration processes [94]. As a result, these calculations give a quantitative assessment of the metasomatic processes that contribute to skarn formation. The isocon method, developed by Grant [95], assesses the impact of hydrothermal alteration by comparing unaltered and least-altered protoliths to mineralogical and geochemical changes. Gresens [41] proposed this approach, excluding the concurrent volume increases and decreases, allowing for the evaluation of elemental mass gain or loss. Grant [95] and Grant [40] enhanced Gresens' equations by assuming immobile elements that do not undergo mass transfer during alteration processes. Utilizing Gresens' equations and isocon diagrams and by picking immobile components, Coelho's GEOISO-Windows™ program of Coelho [39] evaluates and graphs mass balance/volume change by the ultimate mobility of the elements. Al_2O_3 , TiO_2 , Nb, and Y are four immobile elements that appear to have higher correlation coefficients than the other immobile elements, with values of 0.986, 0.981, 0.973, 0.971, and 0.965 for Al_2O_3 vs. Y, Al_2O_3 vs. Nb, TiO_2 vs. Y, TiO_2 vs. Nb, and TiO_2 vs. Al_2O_3 , respectively.

The isocon diagrams (Figure 19) and mass balance analyses (gain or loss) of the elemental compositions of the several skarn zone samples show that each alteration zone has significantly added and depleted major, trace, and rare earth elements (REE) (Table 15). The endoskarn is distinguished microscopically by andradite formation, which is followed by epidote during metasomatism with magnetite and pyrite (see Figure 6). During the endoskarn formation, SiO_2 , MgO , Na_2O , and K_2O were removed from the igneous rock, while Fe_2O_3 , CaO , MnO , Cr_2O_3 , SO_3 , and volatiles (expressed as LOI) were added (Figures 19a and 20). The added Fe_2O_3 , FeO , CaO , and MnO were absorbed by newly formed andradite, but the lost SiO_2 , Na_2O , and K_2O might be attributed to feldspar partial destruction. Except for Au, Sr, W, and Eu, the majority of the trace and all the REE elements were added during endoskarn formation (Figure 19a, Table 15). This zone has lower values for mass (MC) and volume changes (VC) of 4.7% and 1.9%, respectively. The petrographic composition of the proximal Skarn zone is dominated by andradite and magnetite in the prograde subzone and grossular, actinolite, and clinopyroxene remnants in the retrograde subzone. As a result, its geochemical signature based on mass balance calculation is distinguished by enrichment in Fe_2O_3 , FeO , CaO , MnO , MgO , SiO_2 , SO_3 , LOI, and occasionally Cr_2O_3 (Figures 19b and 20a and Table 15). It is distinguished by the higher enrichment of Au, S, Ni, Sr, and W compared to the other skarn zones, as well as additions of Ag, Bi, Co, Cu, Sb, and Te and depletion of all REEs except Lu (Figures 19b and 20b and Table 15). This zone has higher MC and VC values of 68.1% and 69.0%, respectively. However, moderate enrichments of Fe_2O_3 , FeO , CaO , MnO , MgO , SiO_2 , SO_3 , LOI, and Cr_2O_3 with Au, Ag, Bi, Co, Cu, Mo, Ni, S, Sb, Te, W, Zn, and some REE (i.e., Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu) and the depletion of Na_2O , K_2O , Nb, Sr, and light REE (i.e., La, Ce, Pr, and Sm) characterize the intermediate skarn zone (Figures 19 and 20 and Table 15). This refers to the progressive shift from the high-temperature, magma-influenced proximal zone to the cooler, more distant retrograde zone, including andradite, grossular, pyroxenes, and calcite with epidote, scapolite, and chlorite. The significant prevalence of epidote alteration is responsible for the Sr depletion in this intermediate zone [96]. The MC and VC values in this zone are 6.2% and 6.8%, respectively. The distal zone, on the other hand, exhibits SiO_2 , Fe_2O_3 , FeO , CaO , MnO , Cr_2O_3 , SO_3 , and LOI enrichment and MgO , Na_2O , K_2O , TiO_2 , and P_2O_5 depletion (Figures 19d and 20b and Table 15). The enrichments of Ag, As, Bi, Co, Cu, In, Mo, Pb, Sb, Sn, Te, Zn, and Eu are significantly greater than in other skarn zones with the addition of heavy REE (i.e., Tb, Dy, Ho, Er, Yb, and Lu) and depletions of Nb, Sr, and light REE (i.e., La, Ce, Pr, Sm, and Gd) (Figures 19d and 20b and Table 15). The MC and VC values in this zone are moderate values of 20.9% and 22.3%, respectively.



	Endoskarn		Proximal		Intermediate		Distal	
	(Mfi-Moi)/Mo	(Mfi-Moi)/Moi	(Mfi-Moi)/Mo	(Mfi-Moi)/Moi	(Mfi-Moi)/Mo	(Mfi-Moi)/Moi	(Mfi-Moi)/Mo	(Mfi-Moi)/Moi
SiO ₂	−13.89	−0.23	201.93	3.30	8.28	0.14	97.94	1.60
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃	2.99	12.98	11.62	50.52	1.18	5.15	3.53	15.33
FeO	51.09	13.00	199.36	50.73	20.17	5.13	60.29	15.34
MgO	−1.47	−0.58	18.97	7.50	1.98	0.78	−1.48	−0.58
CaO	1.49	0.28	182.39	33.71	24.41	4.51	27.71	5.12
Na ₂ O	−2.91	−0.88	−3.24	−0.98	−2.55	−0.77	−3.25	−0.98
K ₂ O	−3.32	−0.75	−4.29	−0.96	−2.47	−0.56	−3.50	−0.79
TiO ₂	0.13	0.20	−0.33	−0.50	0.12	0.18	−0.41	−0.61
P ₂ O ₅	0.04	0.13	−0.14	−0.45	−0.09	−0.29	−0.18	−0.58
MnO	0.24	2.71	5.75	63.88	0.80	8.92	2.18	24.26
Cr ₂ O ₃	0.14	14.17	0.75	75.17	0.04	4.05	0.22	22.07
SO ₃	2.86	40.83	33.95	485.03	3.97	56.73	1.22	17.36
LOI	8.63	8.90	76.81	79.18	9.64	9.94	25.06	25.84
Ag	2.16	4.50	4.60	9.58	5.43	11.31	24.73	51.52
As	445.39	32.99	1322.41	97.96	223.64	16.57	2347.66	173.90
Au	−0.01	−0.13	1.03	14.72	0.01	0.20	0.42	6.06
Bi	7.53	18.84	55.12	137.80	3.47	8.68	62,482.13	1562.05
Co	149.47	5.94	273.06	10.84	12.17	0.48	675.49	26.83
Cu	980.49	37.13	2760.42	104.52	494.67	18.73	29,772.43	1127.32
In	1.42	35.41	0.81	20.16	0.95	23.84	4.18	104.44
Mo	39.26	15.96	57.80	23.50	18.49	7.52	82.03	33.34
Nb	−0.72	−0.04	3.62	0.22	−1.34	−0.08	−8.49	−0.52
Ni	236.29	16.00	1060.56	71.81	151.86	10.28	378.53	25.63
Pb	0.13	0.00	78.82	1.09	5180.68	71.46	75,629.67	1043.17
S	11,462.33	43.40	1359.79	514.90	15,930.78	60.32	4898.88	18.55
Sb	14.92	20.16	34.64	46.81	9.95	13.45	120.32	162.60
Sn	24.06	25.60	20.13	21.42	23.39	24.88	44.96	47.83
Sr	−472.19	−0.82	35.63	0.06	−275.25	−0.48	−409.32	−0.71
Te	3.24	323.63	7.78	777.61	3.27	327.34	21.97	2196.82
W	−61.74	−0.33	1028.77	5.53	1.74	0.01	468.59	2.52
Zn	79.22	1.43	881.22	15.96	1019.72	18.46	26,462.17	479.13
La	53.70	1.21	−33.32	−0.75	−12.91	−0.29	−12.44	−0.28

Table 15. Cont.

	Endoskarn		Proximal		Intermediate		Distal	
	(Mfi-Moi)/Moi	(Mfi-Moi)/Moi	(Mfi-Moi)/Moi	(Mfi-Moi)/Moi	(Mfi-Moi)/Moi	(Mfi-Moi)/Moi	(Mfi-Moi)/Moi	(Mfi-Moi)/Moi
Ce	71.82	0.85	−65.40	−0.77	−22.60	−0.27	−51.18	−0.60
Pr	4.22	0.45	−7.03	−0.74	−1.72	−0.18	−2.73	−0.29
Sm	0.59	0.09	−4.59	−0.67	−0.57	−0.08	−0.81	−0.12
Eu	−0.09	−0.05	−1.24	−0.68	0.02	0.01	2.62	1.43
Gd	0.60	0.11	−2.26	−0.41	0.50	0.09	−0.14	−0.03
Tb	0.16	0.20	−0.29	−0.37	0.13	0.16	0.06	0.07
Dy	0.61	0.15	−0.86	−0.21	0.94	0.23	0.47	0.12
Ho	0.09	0.12	0.00	0.00	0.20	0.26	0.16	0.21
Er	0.18	0.08	−0.17	−0.08	0.49	0.21	0.25	0.11
Yb	0.03	0.01	−0.31	−0.14	0.15	0.07	0.07	0.03
Lu	0.01	0.03	0.03	0.09	0.01	0.03	0.02	0.06
Mass Change	4.72		68.10		6.24		20.94	
Volume Change	1.95		68.96		6.83		22.26	

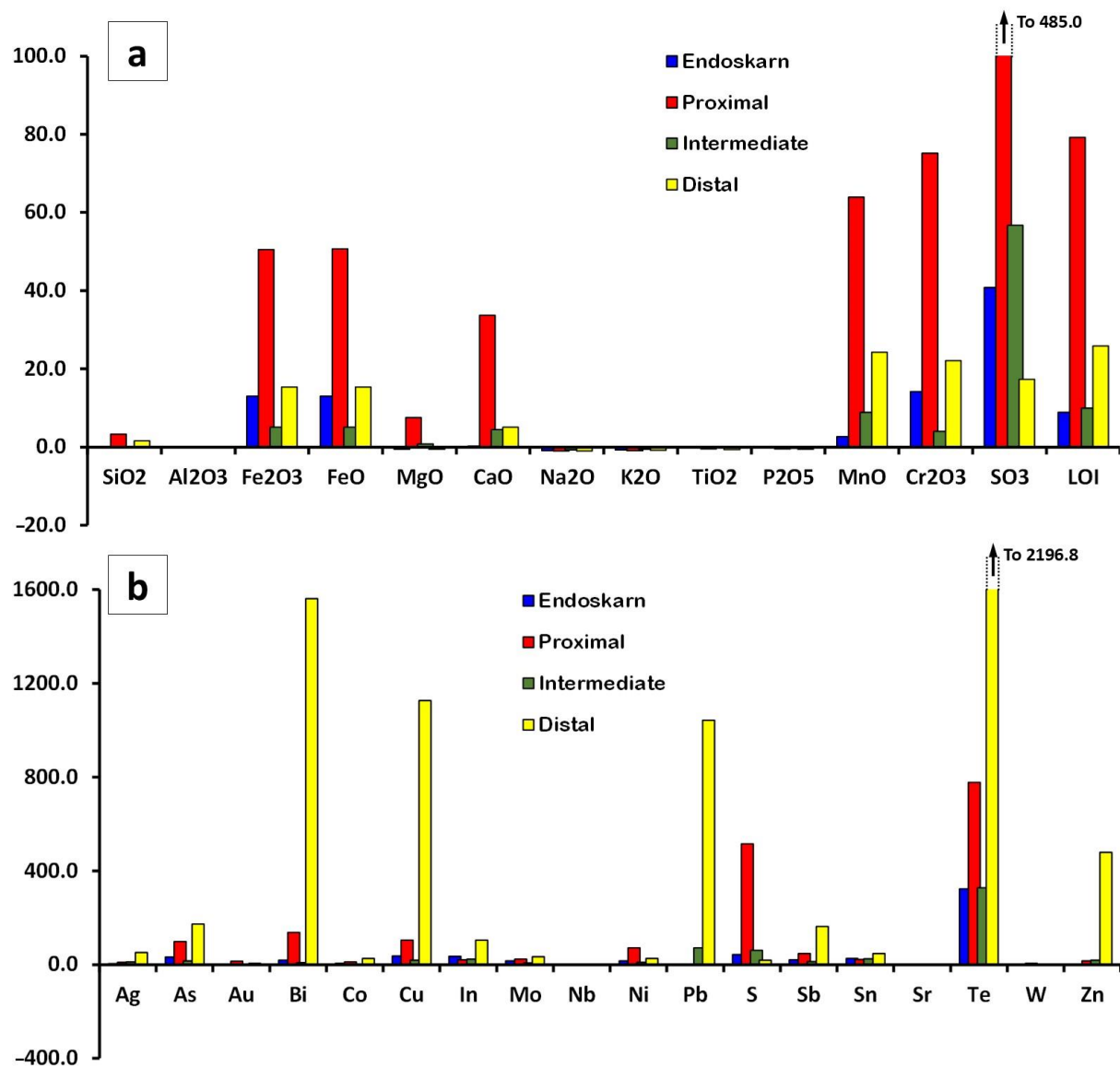


Figure 20. Gain/loss of (a) main oxides (wt.%) and (b) certain selected trace elements associated with skarn deposits (ppm) during alteration in the various skarn zones, using the mean values of the least altered samples as a reference for calculations.

6.2. Yolindi Cu-Fe Skarn Evolution Processes

Fe-skarns are prevalent in the Biga Peninsula, where Cu is pervasive in veins or erratic pockets cutting across magnetite ore bodies in the Fe-skarn deposits. Inextricably connected to the formation of skarns is the emplacement of subvolcanic–plutonic rocks, particularly granitoids such as quartz monzonite, diorite, and monzodiorite, into tertiary sedimentary to volcanosedimentary rocks such as phyllite, meta-carbonates, marble, hornfels, and metabasalt [5]. The majority of these granitoids are oxidized I-type and range in age from Late Eocene–Oligocene to Miocene, and they are emplaced simultaneously with or alongside related porphyry deposits [5]. In the Yolindi area, the formation of skarn mineralogy in association with several metals, including Fe and Cu and their related metals, occurs due to the metasomatic reactions between invaded magmatic fluids from the causative Şaroluk granitoid pluton and the surrounding Torasan Formation country rocks during the skarnification process of the studied Cu-Fe skarn deposit. The intrusion of the I-type Şaroluk quartz monzonite pluton into the Torasan Formation releases Cu- and Fe-bearing magmatic fluids, which react with the Torasan Formation, generating calcium-rich silicate minerals (skarn mineralogy), such as garnet and pyroxene. The early reactions frequently result in prograde skarn minerals such as garnet (mostly andradite with less grossular variants) and pyroxenes [3]. Some of the original skarn minerals can undergo retrograde alteration when the system cools and/or is exposed to external fluids, creating epidote, actinolite, and chlorite, as well as different copper and iron minerals including chalcopyrite, bornite, magnetite, and hematite. Finally, the distal zone may oxidize, resulting in the production of both cerussite and malachite minerals and perhaps increasing the grade of the deposit.

According to the field relationships, along with the mineralogical and petrographic data, as well as the comprehensive paragenetic relationships among the metamorphic/metasomatic and ore mineral phases, the genesis of the Yolindi Cu-Fe deposit is, thus, believed to have involved four main phases that correlate to the metamorphic–metasomatic transition (Figure 21). These four phases started with (1) the metamorphic–bimetasomatic (quasi-isochemical contact metamorphism) stage, (2) the prograde metasomatic stage, and (3) the retrograde metasomatic stage. After these metamorphic–metasomatic stages, a (4) post-metasomatic stage was identified as the weathering and oxidation stage, which can be illustrated by the production of supergene minerals including cerussite, malachite, and goethite (Figure 21).

6.2.1. Contact Metamorphic–Bimetasomatic Stage

Bimetasomatism refers to a sequential metamorphic process in which a rock experiences two distinct metasomatic events consecutively. In this scenario, a reciprocal interaction occurs between a rock undergoing alteration and the fluid, resulting in a mutual alteration of their respective chemical compositions. The process of simultaneous exchange may result in the evolution of two separate mineral assemblages or zones, with one occurring inside the rock and the other within the fluid pathway or surrounding environment [97]. In the Yolindi area, this is the initial stage in the formation of skarn deposits, whenever high-temperature fluids, typically derived from the Early Miocene Şaroluk granitoid (MŞ) intrusion, react with the Upper Paleozoic Torasan Formation (Pzt), causing contact metamorphism and bimetasomatism, leading to significant mineralogical and textural changes. This intrusion that triggered contact metamorphism in the Upper Paleozoic Torasan Formation (Pzt) was initially emplaced at the beginning of this stage. The volatile-rich felsic melt and heat flow from the Şaroluk intrusion had isochemically metamorphosed the Torasan and nearby Karakaya Formation country rocks, which had then bimetasomatized into skarnoid-hornfels, having quartz, clinopyroxene, and re-crystallized calcite (see Figure 3) in intercalations of biotite schists and phyllite of the Torasan Formation. At this stage, no sulfides or oxide disseminations were seen or developed.

		Isochemical contact metamorphism- bimetasomatic stage	Prograde metasomatic stage	Retrograde metasomatic stage	Post- metasomatic stage
Metamorphic & Alteration minerals	Clinopyroxene	██████████			
	re-crystallized calcite	██████████			
	Andradite		██████████		
	Andradite-grossular		██████████		
	Augite	██████████	██████████		
	Hedenbergite		██████████	██████████	
	Scapolite		██████████	██████████	
	Epidote		██████████	██████████	
	Biotite	██████████	██████████		
	Chlorite		██████████	██████████	
	Actinolite		██████████	██████████	
	Calcite		██████████	██████████	
	Sericite			██████████	
	Quartz		██████████	██████████	
Mineralization	(primary)	Magnetite	██████████	██████████	
		Spec. Hematite		██████████	
		Chalcopyrite		██████████	
		Pyrite	██████████	██████████	
		Galena		██████████	
		Sphalerite		██████████	
	Oxid. Supergene	Cerussite			██████████
		Malachite			██████████
		Goethite			██████████

Figure 21. A comprehensive paragenetic relationship among the metamorphic/metasomatic and ore mineral phases during the different stages of metasomatism and mineralization in the Yolindi Cu-Fe skarn deposit.

6.2.2. Prograde Metasomatic Stage

It may be assumed that their magma cooled and solidified more quickly, allowing the residual liquid to become more silicic and volatile-rich in the late stage of magmatic differentiation. This would explain why microgranophyre patches formed in a larger body of Saroluk quartz monzonite in the Yolindi area (see Figure 4). A fine-grained texture can arise from this quick cooling, which can “quench” the minerals and inhibit them from becoming larger crystals [98]. Consequently, the quick fluid escape indicated that this was probably related to pressure-quench crystallization [32]. In general, as the magma that formed Şaroluk granitoid rocks cools and crystallizes, volatile chemicals such as water, carbon dioxide, fluorine, and chlorine are released, generating a magmatic-hydrothermal fluid [3,99]. This fluid is rich in metals such as Cu, Fe, and others, in addition to numerous elements. During the prograde metasomatic stage, it interacts with the surrounding Torasan Formation country rock, which is typically composed of phyllite and schists with serpentized peridotites (Pzts) and marble members (see Figure 3). Furthermore, the resurgent boiling of the prograde metasomatic stage, along with the progressive crystallization of the Şaroluk granitoid rocks, causes degassing of the volatile phases, as well as a large volume of highly evolved magmatic-hydrothermal solution that became saturated in the magma and began to exsolve as a separate phase [100]. When these exsolved fluids penetrate country rocks, they cause abrupt and rapid hydrofracturing in the crystallizing magma (Şaroluk granitoid rocks) and the nearby wall or host rocks

(Torasan Formation). This hydrofracturing is also a consequence of bimetasomatic and decarbonation alteration events [101], which form regions of distinct skarn zones in the study area: endoskarn and multiple exoskarn zones.

In the Yolindi area, the prograde metasomatic alteration is represented by a series of medium- to coarse-grained Fe-rich anhydrous calc-silicate minerals (andradite and augite), with magnetite and pyrite formed in the endoskarn and proximal exoskarn zones, where Fe_2O_3 , CaO , MnO , Cr_2O_3 , SO_3 , and volatiles (expressed as LOI) were added (mass balance calculation data). Andradite in these two zones is more Fe-rich than andradite in the intermediate zone. Furthermore, the presence of un-zoned andradite in the endoskarn (Figure 15a) and zoned andradite in the proximal exoskarn (Figure 15b) can provide data regarding skarn formation conditions, fluid flow dynamics, and element mobility. Un-zoned andradite (Figure 15a) forms under stable conditions such as constant temperature and pressure and is uniform from core to rim (Table 3). It might point to rapid crystallization in the endoskarn, which did not allow for compositional zoning to develop. Zoned andradite (Figure 15b), on the other hand, shows compositional shifts from core to rim, indicating differences in formation conditions. This is prevalent in proximal exoskarns, which form when an intrusive body interacts with the nearby Torasan Formation country rocks. The zonation often recorded variations in temperature, pressure, and fluid composition as magmatic fluids moved outward from the intrusion and interacted with wall rocks [102]. Furthermore, the presence of zoned andradite indicates an extended period of skarn formation, which allowed for the sequential deposition of different garnet compositions as conditions changed [102]. Exoskarn zoning patterns have the potential to provide insight into fluid flow and source evolution during the formation of skarns [3,102]. In general, a metasomatic front moving through the rock is typically to blame for garnet zoning. As the fluids arrive, the country rock gradually reacts with them, leaving a record of this reaction in the form of garnet zoning [102]. While clinopyroxene is represented by augite, which is formed at high temperatures in the endoskarn and proximal zones during skarn formation due to its proximity to a heat source, augite forms earlier in the paragenetic sequence, indicating more temperature stability under reducing conditions, implying a more reducing environment [103]. Magnetite, which exhibits magmatic-hydrothermal affinities in the endoskarn and proximal zones, having a higher TiO_2 value with an average of 0.11 wt.% and 0.02 wt.%, respectively (Figure 18b,c and Table 13), is formed along with pyrite during this stage.

6.2.3. Retrograde Metasomatic Stage

The retrograde metasomatic stage outlines the reactions that occur when the system cools and the original anhydrous calc-silicate (prograde) mineral assemblages (e.g., andradite and augite) are replaced by new hydrous calc-silicate (retrograde) mineral assemblages (e.g., epidote and actinolite) due to changes in physical–chemical conditions such as temperature, pressure, and fluid composition [3,104]. It also entails the insertion of additional fluid phases, such as late magmatic fluids exsolved from the cooling intrusion and exogenous fluids (typically meteoric fluid), into the system through fractures and other permeable pathways [1]. The redox conditions of the infiltrating fluids may differ from those of the original magmatic fluids. Meteoric water, for example, is frequently more oxidizing than magmatic fluids. The shift in redox conditions could cause the previously formed prograde minerals to become unstable, break down, and evolve into new mineral phases [105]. Actinolite, epidote, scapolite, calcite, and chlorite in the exoskarn zone of the Yolindi area are suggestive of retrograde metamorphism and alteration formed under lower temperature and pressure conditions, as well as a neutral to alkaline pH environment pseudomorph after garnet and pyroxene [106] (see Figures 8, 10 and 15). The andradite–grossular intergrowth that characterizes the garnet at the retrograde stage in the proximal retrograde and intermediate zones (see Figure 15c–e), which refers to a drop in temperature where andradite is stable at higher temperatures [107] while grossular prefers to develop at lower temperatures [108], offers crucial hints concerning the transition from andradite to grossu-

lar. This transition implies a change in the composition of the hydrothermal fluids, which become more neutral to alkaline in character; specifically, a drop in iron and an increase in aluminum imply a shift from $\text{Adr}_{77}\text{Grs}_{20}\text{Alm}_1$ (Fe-rich) to $\text{Adr}_{59}\text{Grs}_{39}\text{Alm}_1$ (Al-rich) (see Table 3). This implies that the system was cooling and evolving, probably with declining magmatic impact and maybe increasing meteoric water input. Additionally, at this period, the pressure conditions remained mostly constant [109]. Additionally, Hedenbergite was identified in the retrograde intermediate zone in association with scapolite (see Figure 15f), implying that this zone underwent lower temperatures, most likely because of its distance from the intrusive heat source. It usually occurs under more oxidizing conditions than augite. Because of the effect of meteoric water mixing with magmatic fluids, the shift from augite to hedenbergite throughout a skarn system may, therefore, record a move from more reducing to more oxidizing environments [1,110]. Moreover, the interaction of fluid–rock in Cl-rich environments is shown by the formation of Cl-rich scapolite with hedenbergite, which shows extensive metasomatic alteration and the mobilization of elements, including Ca, Fe, Na, and Cl (mass balance calculation data) from the Şaroluk quartz monzonite and Torasan production, to re-concentrate into these minerals. In the exoskarn zone, magnetite and late Cl-rich scapolite (Table 5) indicate brines are essential for Fe transfer and metasomatism throughout the fluid pathway [111]. Chamosite, which mostly represents the chlorite mineral in the study area (see Figure 17g), is often stable at lower temperatures, decreasing from proximal ($T = \text{an average of } 286\text{ }^{\circ}\text{C}$) to distal ($T = \text{an average of } 152\text{ }^{\circ}\text{C}$) over the intermediate zone ($T = \text{an average of } 179\text{ }^{\circ}\text{C}$) (Table 9). Its formation frequently indicates the stability of the skarn system after high temperatures. It can be associated with ore minerals such as chalcopyrite, sphalerite, or galena in the study area, suggesting a proximity to sulfide mineralization zones. The Fe-rich composition of chamosite implies special redox conditions with relatively low oxygen fugacity [112]. Along with epidote, actinolite, calcite, and quartz in the proximal retrograde and intermediate zones, the presence of small magnetite crystals (partially martitized to hematite) within the garnet and clinopyroxenes (see Figure 8) proves that magnetite was formed after garnet and clinopyroxene during this retrograde stage. This magnetite, whose TiO_2 content averages 0.01 wt.%, is of hydrothermal metasomatic origin and resembles the world-class skarn of Xie, et al. [113] (see Figure 18b,c). A variety of copper and iron minerals, such as chalcopyrite, bornite, magnetite, and specular hematite, are formed during this phase when the system cools and is exposed to external fluids (see Figures 8 and 10).

6.2.4. Post-Metasomatic Stage

The presence of cerussite and malachite in the distal exoskarn zone of Cu-Fe skarn deposits, common in oxidation zones, indicates that the deposit has undergone weathering and oxidation, converting primary sulfide minerals into secondary oxide and carbonate minerals (see Figures 10 and 21). The formation of these minerals suggests metal leaching and movement from proximal areas, where they dissolve primary metal sulfides, transport them outward, and precipitate them as carbonates due to pH changes and redox conditions, suggesting the skarn system developed in a carbonate-rich environment while the neutralization of acidic fluids occurred. Additionally, the presence of these minerals in the distal exoskarn zone can aid in the modeling of past fluid flow pathways, indicating active mineralizing fluids that could be useful for exploration targeting.

6.3. Comparison of the Genetic Relationship between the Yolindi Cu-Fe Skarn and Calc-Alkaline Magmatism in the Biga Peninsula with Other Worldwide Skarns

The genetic relationship between Cu-Fe skarn deposits and magmatic activity in skarn systems may be relevant to other skarn deposits throughout the world, including those in the Biga Peninsula in northwestern Turkey (Table 16). In general, the distribution, mineralogy, and metal ratios of skarns are extremely diverse, as described by Einaudi, et al. [114], and may correspond to the magma types, depth of formation, oxidation state, and distance from intrusion [115]. A metallogenic province cannot form without the various oxygen

fugacities residing in the magma and the released ore solution. In this context, the more mafic igneous rock types of an oceanic island arc gave rise to a magnetite-rich skarn, which is analogous to the Fe-Co skarn of Smirnov, et al. [116], with a considerable Cu, Co, and Au content [114]. In contrast, hypabyssal settings generate different skarns, such as Fe, Cu, Mo, Pb, and Zn. Highly siliceous alkalic granite belts have lithophile mineralized skarns (such as Sn, W, F, Li, Be, and B), whereas moderately siliceous magmas contain litho-chalcophile mineralization, which includes W, Ho, Cu, Zn, Pb, Au, Hg, and Sb. Magnetite-bearing epidote, pyroxene, plagioclase, garnet endoskarn, and garnet-epidote-bearing exoskarn are the main constituents of an island-arc skarn [114]. The main mineral prevalent in skarns is andraditic garnet, whereas pyroxene is a member of the diopside–hedenbergite association. The main major iron oxide mineral, magnetite, can be formed between the exoskarn and calcareous rocks or between the endoskarn and exoskarn. As shown at the Shinyama mine in the Kamaishi area, Japan [117], chalcopyrite and pyrite are major sulfide minerals. Epidote, actinolite, chlorite, calcite, and quartz are some of the minerals that are most representative of retrograde alteration. According to Meinert [118], copper skarns from oceanic island-arc settings associated with quartz monzonite to granodiorite plutons exhibit high garnet to pyroxene proportions, comparatively oxidized assemblages (andraditic garnet, diopside, pyroxene, magnetite, and hematite), and a medium to significant sulfide content.

The EPMA data for garnet reveal that it is primarily classified as magmatic garnet (Type D), which is typically derived from metasomatic rocks (e.g., skarns) (see Figure 16a). It is mostly compatible with garnet from other worldwide Cu-Fe skarn deposits, with a little Zn skarn deposit from Meinert, et al. [1] (see Figure 16b), as well as garnet from the Ayazmant Fe-Cu skarn of Turkey of Oyman [119], the Ahar Fe-Cu skarn deposit of Iran of Mollai, et al. [120], the Kamaish Fe skarn of Japan of Einaudi and Burt [121] (Figure 22a₁). Furthermore, the analyzed clinopyroxenes are mostly compatible with clinopyroxene from the Ayazmant Fe-Cu skarn of Turkey of Oyman [119], the Evciler Cu-Au skarn of Turkey of Öztürk and Helvacı [122] (Figure 22a₂), and other worldwide Cu-Fe skarn deposits of Meinert, et al. [1] (Figure 16d). The analyzed samples of the Şaroluk quartz monzonite rocks are associated with the studied Yolindi Fe-Cu skarn plot in the area between plutons associated with Fe and Cu skarns on the TiO₂ vs. Zr diagram, as proposed by Meinert [115], Oyman [119], and Mollai, et al. [120], shown in Figure 22b. Meinert [115] noticed that practically no skarn-related plutons would be categorized as peralkaline based on Al saturation and that the majority of their compositions cluster close to the boundary between metaluminous and peraluminous. The Şaroluk quartz monzonite, which is categorized as a metaluminous I-type granitoid due to the considerably greater A/NK and lower A/CNK values, is plotted in nearby areas of the Cu and Zn skarns of Meinert [115] and the Evciler Fe-skarn granitoids of Öztürk, et al. [123] (Figure 22c). The MgO content of the Şaroluk quartz monzonite ranges from 1.97 wt.% to 3.59 wt.% with an average of 2.53 wt.%; however, this value is 3% for Fe-skarn granitoids, 3.2% for Au-skarn granitoids, and 1.8% for Cu-skarn granitoids [115]. The Şaroluk quartz monzonite samples plot close to the Fe-, Cu-, and Au-skarn granitoids in the SiO₂ vs. MgO binary diagram, which are comparable with the Evciler Au-Cu skarn granitoids of Öztürk, et al. [123] (Figure 22d). According to Figure 22e, which depicts the relationship between Y and Nb, the majority of skarn-associated plutons occur in volcanic arcs (VAG) and syn-collision (Syn-COLG) granitoids and within continental plates (WAG) [1]. Sn, W, and most Mo skarns are solely linked with plutons that plot in the WPG field, whereas Fe, Au, Cu, and Zn skarns are only associated with plutons that plot in the VAG + Syn-COLG field [1]. The studied samples of the Şaroluk granite fall in the field of VAG and Syn-COLG near to the Cu- and Fe-skarns of Meinert [115] and exhibit a similar pattern to the Evciler Au-Cu skarn granitoids of Öztürk, et al. [123] and the Ahar Fe-Cu skarn granitoids of Mollai, et al. [120] (Figure 22e). It is clear from the discussion and comparison above that the island-arc environment is ideal for the Cu-Fe skarn deposits in the Yolindi area and the ore solution associated with their magmatic genesis.

Table 16. Comparison of Cu-Fe skarn deposits in the Yolindi area of NW Turkey with other skarn deposits in Turkey and across the world.

Skarn Type	Location N	Name	Host rock	Associated Igneous Rock	Composition	Age of Magmatism	ProGrade Minerals	RetroGrade Minerals	Ore Minerals	Grade	Accompanying Metal	References
Fe, Cu	Çanakkale, Turkey	Yolindi	Torasan formation (phyllite, Schists, hornfels)	Şaroluk pluton	Granodiorite, quartz monzonite	Early Miocene	adr, aug	grs, ep, act, hd, scp, chl, ser, cal, qz	mag, hem, py, ccp, gn, cer, sp, mal		Pb, Zn	The current study
Fe	Balikesir, Turkey	Yasyeri	Meta pelitic rocks, carbonate lenses	Eybek pluton	Granite, granodiorite	23–26 Ma	di, hd	ep, cal	mag, hem, ccp, py, sp, gn	30%–50%	Cu	Karaaslan and Başarı [124]
Pb, Zn, Cu	Balikesir, Turkey	Bağırkaç	schist with metacarbonate lenses in Karakaya complex	Eybek pluton	Granite, granodiorite	23–24 Ma	Wo, adr, grs, di, scp	cal, tr	sp, gn, hem, ccp, py	10% Pb + Zn	Cu	Gümüş [125], Dora [126], Önal, et al. [127]
Fe, Cu	Balikesir, Turkey	Şamlı	Karakaya complex	Şamlı pluton	Granodiorite, diorite, granite porphyry	23 Ma	adr-grs, di-hd	act, ep, cal, tr	mag, hem	58.5%	Au, Cu	Tamer and Kurt [128]
Cu, Au	Çanakkale, Turkey	Evciler	Metamorphics of Kazdag massif	Evciler pluton	Granodiorite, qtz diorite	26 Ma	adr, di grs, di-hd, scp, py	ep, cal, tre, chl, qt	mag, hem, ccp, py	52%	Au, Cu	Öztürk, et al. [123], Öztürk, et al. [129]
Pb, Zn	Çanakkale	Bergaz	Permian limestones in Bozalan formation	Kestanbol pluton	Monzodiorite, granodiorite	19 Ma	adr, jhn, di, hd	ep, cal, chl	mag, hem	49.98%	Fe	Gjelsvik [130]
Fe, Cu, Pb	Çanakkale, Turkey	Uskufcu (Aladag)	Permian, bozalan carbonates	Kestanbol pluton	Monzonite, qtz monzonite	19 Ma	di, gro, jhn	ep, tr, act	gn, sp, mag, ccp		Pb-Zn	Arik and Aydin [131]
Fe, Cu	Çanakkale, Turkey	Bakırlık	Oligocene sedimentary rocks	Halilaga subvolcanic domes	Diorite porphyry	26 Ma	grt, hd	ep, chl, act	ccp, mag		Fe	Öngen, et al. [132]
Pb, Zn	Çanakkale, Turkey	Handere	Metacarbonates in Kazdag massif	subvolcanic andesitic rocks	Andesite porphyry	Oligocene	grt, jhn	ep, cal, qz	sp, gn	3.25% Pb, 1.75% Zn	Cu	Mesut [133]

Table 16. Cont.

Skarn Type	Location N	Name	Host rock	Associated Igneous Rock	Composition	Age of Magmatism	ProGrade Minerals	RetroGrade Minerals	Ore Minerals	Grade	Accompanying Metal	References
Pb, Zn	Çanakkale, Turkey	Karaaydın	Metacarbonates in Kazdag massif	Eybek pluton, subvolcanic andesitic rocks		Oligocene	wo, di-hd, adr-grs	ep, chl, cal, qz	gn, sp, py, po	8.48% Pb + Zn		Tufan [134], Yücelay [135]
Fe–Cu	Balıkesir, Turkey	Ayazmant (Ayvalık)	Hornfels, skarn	Granodioritic to monzodioritic porphyries			di, adr-grs, scp	ep, amp, py, or, chl, cal, qz	mag, ccp, py, bn, mol, gth, hem, po, gn, sp, various Au-Ag- Te-Se	46% Fe and 0.6% Cu		Oyman [119]
Cu, Fe	Alborz, Iran	Ahar	Impure carbonate and granodiorite	Granodiorite	Granodiorite		pyx, grt	ep,chl, cal, ser	ccp, py, mag, hem	1.2% Cu and Fe		Mollai, et al. [120],Mollai [136]

Abbreviations: actinolite (act), andradite (adr), amphibole (amp), augite (aug), bornite (bn), calcite (cal), chalcopyrite (ccp), chlorite (chl), diopside (di), epidote (ep), galena (gn), grossular (grs), garnet (grt), goethite (gth), hedenbergite (hd), hematite (hem), johannsenite (jhn), magnetite (mag), malachite (mal), molybdenite (mol), orthoclase (or), pyrrhotite (po), pyrite (py), pyroxene (pyx), quartz (qz), scapolite (scp), sericite (ser), sphalerite (sp), tremolite (tr), wollastonite (wo).

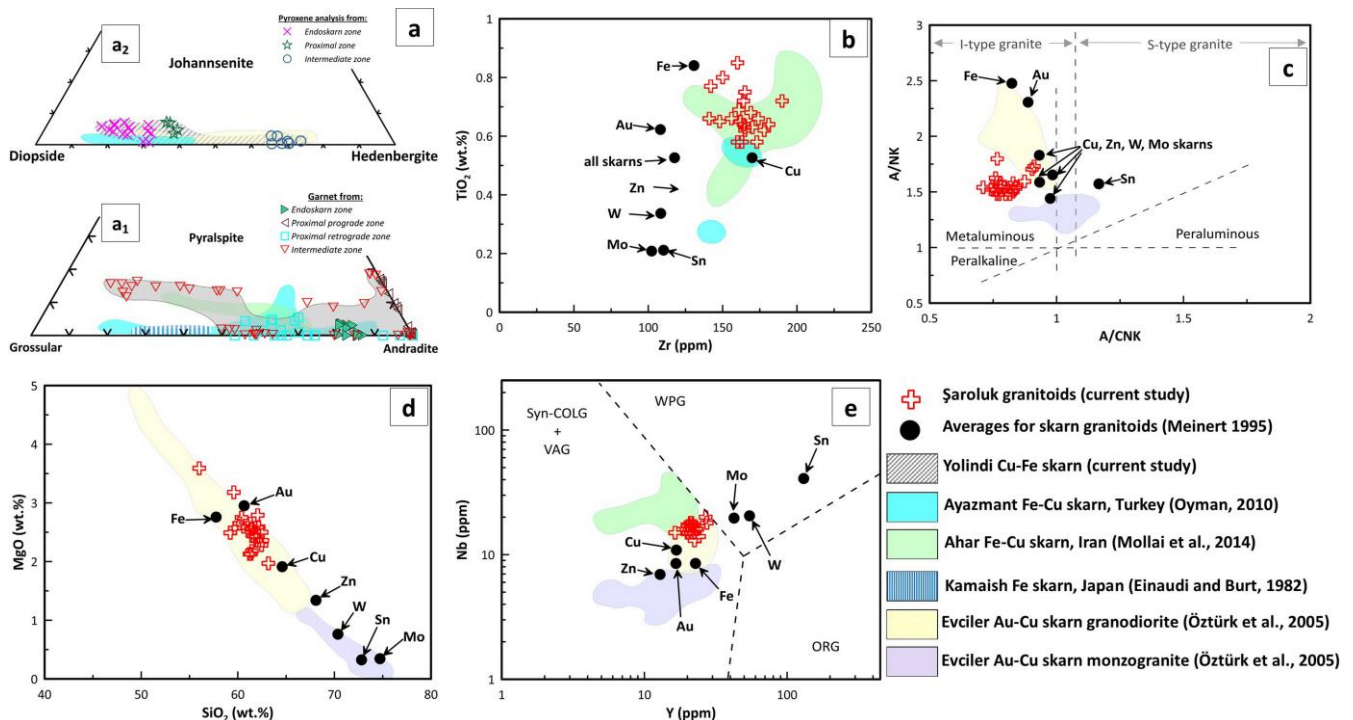


Figure 22. (a) Ternary diagram comparing the composition of garnet (a₁) and pyroxene (a₂) from the Yolindi area to skarn deposits in different regions of the world. (b) The variation diagram of Zr vs. TiO_2 depicts the relationship between igneous rocks of the Şaroluk quartz monzonite and those associated with the Yolindi Cu-Fe skarn deposit compared to other igneous rocks related to skarn deposits according to Meinert [115], Oyman [119], and Mollai, et al. [120]. (c) A/NK vs. A/CNK, (d) MgO vs. SiO_2 , and (e) Nb vs. Y diagrams for the Şaroluk quartz monzonite and comparison with other world skarn granitoids according to Meinert [115], Öztürk, et al. [123], and Mollai, et al. [120].

7. Conclusions

The Yolindi Cu-Fe Skarn deposit in the Biga Peninsula is the result of the intrusion of subvolcanic-plutonic rocks, particularly granitoids such as quartz monzonite, diorite, and monzodiorite, into tertiary sedimentary to volcanosedimentary rocks such as phyllite, meta-carbonates, marble, hornfels, and metabasalt. During the skarnification process of the studied Cu-Fe skarn deposit, metasomatic reactions between invaded magmatic fluids from the causative Şaroluk granitoid pluton and the surrounding Torasan Formation country rocks result in the formation of skarn mineralogy in association with several metals, including Fe and Cu and their related metals. When the oxidized I-type Şaroluk quartz monzonite pluton intruded into the Torasan Formation, it released magmatic fluids that were rich in copper and iron. These fluids interact with the Torasan Formation to form calcium-rich silicate minerals, including garnet and pyroxene. Early reactions frequently lead to prograde skarn minerals, including pyroxenes (mostly augite with higher diopsidic ratios) and garnet (mostly andradite with fewer grossular variations). When the system cools and/or is exposed to external fluids (meteoric fluids), some of the initial skarn minerals might undergo retrograde alteration, resulting in epidote, actinolite, and chlorite, as well as other copper and iron minerals including chalcopyrite, bornite, magnetite, and specular hematite. Finally, the distal zone could oxidize, forming the minerals malachite and cerussite and perhaps raising the grade of the deposit. As a result, four primary phases are thought to have been involved in the formation of the Yolindi Cu-Fe deposit: the metamorphic–bimetasomatic (quasi-isochemical contact metamorphism) stage, the prograde metasomatic stage, and the retrograde metasomatic stage. The formation of supergene minerals such as cerussite, malachite, and goethite serves as an example of the post-metamorphic stage known as weathering and oxidation, which follow these

metamorphic–metasomatic processes. Likewise, the andradite–grossular intergrowth, which denotes a change in the composition of hydrothermal fluids, suggests a transition from andradite to grossular in the exoskarn zone of the Yolindi area. It is confirmed that magnetite is developed after garnet and clinopyroxene during the retrograde stage by the presence of tiny magnetite crystals (partially martitized to hematite) within the garnet and clinopyroxenes in the proximal retrograde and intermediate zones.

Taking all factors into account, genetic relationships between Cu–Fe skarn deposits and magmatic activity in skarn systems may be relevant for other skarn deposits worldwide, including those on the Biga Peninsula in northwest Turkey. Furthermore, the studied garnet is predominantly magmatic garnet, generated from metasomatic rocks, and is compatible with garnet from global Cu–Fe skarn deposits with a small Zn skarn deposit, according to EPMA data. Additionally, the majority of the studied clinopyroxenes coincide with those from the Turkish skarns Ayazmant Fe–Cu and Evciler Cu–Au. The Şaroluk quartz monzonite rock samples from the studied Yolindi Fe–Cu skarn also match the Fe and Cu skarn plutons of Meinert (1995). Consequently, the Cu–Fe skarn deposits in the Yolindi area and the ore solution associated with their magmatic origin evolved in the island–arc environment.

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Appendix A. XRD Analyses of Representative Samples from the Magnetite Bearing Granodiorite

No.	Ref. Code	Compound Name	Chemical Formula	Semi-Quant (%)		
				BG-209A	BG-220A	Average
1	98-001-8053	Anorthite	$\text{Al}_2 \text{Ca}_1 \text{O}_8 \text{Si}_2$	36	45	40.5
2	98-001-7363	Microcline	$\text{Al}_1 \text{K}_1 \text{O}_8 \text{Si}_3$	24	14	19
3	98-005-6693	Titanite	$\text{Ca}_1 \text{O}_5 \text{Si}_1 \text{Ti}_1$	12	12	12
4	98-002-8097	Actinolite	$\text{H}_2 \text{Al}_{0.23} \text{Ca}_{1.68} \text{Fe}_{0.48} \text{Mg}_{4.59} \text{Na}_{0.1} \text{O}_{24} \text{Si}_{7.92}$	13		6.5
5	98-006-7745	Biotite	$\text{H}_2 \text{Al}_{1.996} \text{Fe}_{2.554} \text{K}_1 \text{O}_{12} \text{Si}_{2.45}$	1	12	6.5
6	98-002-3114	Quartz low	$\text{O}_2 \text{Si}_1$	3	9	6
7	98-002-8260	Ferrohornblende	$\text{H}_2 \text{Ca}_2 \text{Fe}_5 \text{Na}_1 \text{O}_{24} \text{Si}_8$	8		4
8	98-000-5530	Diopside	$\text{Ca}_1 \text{Mg}_1 \text{O}_6 \text{Si}_2$		7	3.5
9	98-007-8202	Magnetite	$\text{Fe}_3 \text{O}_4$	1	1	1
10	98-006-2733	Pyrite	$\text{Fe}_1 \text{S}_2$	1	1	1

Appendix B. XRD Analyses of Representative Samples from the Magnetite Bearing Endoskarn

No.	Ref. Code	Compound Name	Chemical Formula	Semi-Quant (%)
				BG-209D
1	98-002-1810	Epidote	H ₁ Al ₂ Ca ₂ Fe ₁ O ₁₃ Si ₃	83
2	98-006-1164	Andradite	Ca ₃ Fe ₂ O ₁₂ Si ₃	9
3	98-003-4859	Goethite	H ₁ Fe ₁ O ₂	4
4	98-004-1521	Magnetite	Fe ₃ O ₄	2
5	98-007-0044	Hematite	Fe ₂ O ₃	1
6	98-005-4829	Quartz low	O ₂ Si ₁	1

Appendix C. XRD Analyses of Representative Samples from the Proximal Prograde Zone

No.	Ref. Code	Compound Name	Chemical Formula	Semi-Quant (%)				
				BG-35A	BG-41	BG-40	BG-103	Average
1	98-002-8161	Andradite	Ca ₃ Fe ₂ O ₁₂ Si ₃	35	39	44	25	35.75
2	98-000-5164	Chalcopyrite	Cu ₁ Fe ₁ S ₂	7	31	25	31	23.5
3	98-002-3114	Quartz low	O ₂ Si ₁	21	8	11	16	14
4	98-003-5029	Calcite	C ₁ Ca ₁ O ₃	20	12	6	15	13.25
5	98-004-0639	Magnetite	Fe _{2.897} O ₄	10		8	5	5.75
6	98-000-5961	Pyrite	Fe ₁ S ₂	4		6	6	4
7	98-001-2749	Hematite	Fe ₂ O ₃	10				2.5
8	98-005-2707	Clinocllore Ilb-2	H ₂ Al ₂ Mg ₅ O ₁₅ Si ₃	2				0.5

Appendix D. XRD Analyses of Representative Samples from the Proximal Retrograde Zone

No.	Ref. Code	Compound Name	Chemical Formula	Semi-Quant (%)				
				BG-237E	BG-71	BG-253	BSD-12	Average
1	98-005-4829	Quartz low	O ₂ Si ₁	47	79	53	61	60.0
2	98-002-8162	Andradite	Ca ₃ Fe ₂ O ₁₂ Si ₃	24	11	14	6	13.8
3	98-003-8838	Diopside	Al _{0.6} Ca _{0.96} Fe _{0.51} Mg _{0.44} O _{6.12} Si _{1.4}		8	24		8.0
4	98-001-1924	Grossular	Al ₂ Ca ₃ O ₁₂ Si ₃	3		6	13	5.5
5	98-003-5028	Calcite	C ₁ Ca ₁ O ₃	7		3	9	4.8
6	98-004-6522	Hematite	Fe ₂ O ₃	14	2		1	4.3
7	98-008-6291	Bornite	Cu ₂ Fe ₁ S ₂				9	2.3
8	98-006-1953	Goethite	H ₁ Fe ₁ O ₂	5				1.25
9	98-000-5164	Chalcopyrite	Cu ₁ Fe ₁ S ₂				1	0.3

Appendix E. XRD Analyses of Representative Samples from the Intermediate Zone

No.	Ref. Code	Compound Name	Chemical Formula	Semi-Quant (%)				
				BSS-12	BG-217C	BG-35A	BG-103	Average
1	98-002-8162	Andradite	Ca ₃ Fe ₂ O ₁₂ Si ₃	7		26	32	16.3
2	98-000-5543	Epidote	H ₁ Al _{2.16} Ca ₂ Fe _{0.84} O ₁₃ Si ₃	36	23			14.8
3	98-003-5029	Calcite	C ₁ Ca ₁ O ₃	7	8	13	14	10.5
4	98-004-0906	Quartz low	O ₂ Si ₁	7		20	15	10.5
5	98-004-6519	Hematite	Fe ₂ O ₃	3		19	18	10.0
6	98-004-5762	Microcline	Al ₁ K _{0.96} Na _{0.04} O ₈ Si ₃		26			6.5
7	98-007-6432	Clinopyroxene	Al _{0.3} Ca _{0.75} K _{0.23} Mg _{0.75} O ₆ Si _{1.97}		21			5.3
8	98-000-5765	Scapolite	C _{0.87} Al _{8.69} Ca _{4.17} Cl _{0.73} K _{0.46} Na _{3.31} O _{52.09} S _{0.37} Si _{14.99}		21			5.3
9	98-005-2707	Clinocllore Ilb-2	H ₂ Al ₂ Mg ₅ O ₁₅ Si ₃	7		10		4.3
10	98-002-8914	Clinzoisite	H ₁ Al _{2.79} Ca ₂ Fe _{0.21} O ₁₃ Si ₃	15				3.8
11	98-000-5164	Chalcopyrite	Cu ₁ Fe ₁ S ₂	2	1	6	5	3.5
12	98-006-6931	Grossular	Al ₂ Ca ₃ O ₁₂ Si ₃	8				2.0
13	98-007-8261	Goethite	H ₁ Cd _{0.1} Fe _{0.9} O ₂			3	5	2.0
14	98-001-2001	Muscovite 3T	H ₂ Al ₃ K ₁ O ₁₂ Si ₃	5				1.3
15	98-007-8202	Magnetite	Fe ₃ O ₄			5		1.3

Appendix F. XRD Analyses of Representative Samples from the Distal Zone

No.	Ref. Code	Compound Name	Chemical Formula	Semi-Quant (%)		
				BG-76	MTK-5	Average
1	98-001-1941	Muscovite 2M1	H ₂ Al ₃ K ₁ O ₁₂ Si ₃	31		15.5
2	98-008-5903	Dolomite	C ₂ Ca ₁ Mg ₁ O ₆	2	25	13.5
3	98-000-6100	Malachite	C ₃ H ₂ Cu ₂ O ₅	18	7	12.5
4	98-005-4829	Quartz low	O ₂ Si ₁		22	11
5	98-002-1957	Calcite	C ₁ Ca ₁ O ₃		21	10.5
6	98-004-2100	Vesuvianite	H _{7.48} Al _{12.52} Ca ₁₉ Fe _{0.48} O ₇₈ Si ₁₈	16		8
7	98-002-1588	Hemimorphite	H ₄ O ₁₀ Si ₂ Zn ₄	5	10	7.5
8	98-001-7069	Cerussite	C ₁ O ₃ Pb ₁	7	5	6
9	98-000-6278	Hematite	Fe ₂ O ₃	5	5	5
10	98-002-1961	Magnesite	C ₁ Mg ₁ O ₃	5		2.5
11	98-002-1822	Galena	Pb ₁ S ₁	2	2	2
12	98-003-4857	Goethite	H ₁ Fe ₁ O ₂	3		1.5
13	98-007-2188	Sphalerite	S ₁ Zn ₁	1		0.5

References

- Meinert, L.D.; Dipple, G.M.; Nicolescu, S.; Hedenquist, J.W.; Thompson, J.F.H.; Goldfarb, R.J.; Richards, J.P. World Skarn Deposits. In *Economic Geology 100th Anniversary Volume*; Society of Economic Geologists: Littleton, CO, USA, 2005; pp. 299–336.
- Ray, G.; Webster, I. *An Overview of Skarn Deposits: Ore Deposits, Tectonics, and Metallogeny in the Canadian Cordillera*; British Columbia Geological Survey: Victoria, BC, Canada, 1990; pp. 7–55.
- Meinert, L.D. Skarns and Skarn Deposits. *Geosci. Can.* **1992**, *19*, 145–162.
- Meinert, L.D. Skarn zonation and fluid evolution in the Groundhog mine, Central mining district, New Mexico. *Econ. Geol.* **1987**, *82*, 523–545. [\[CrossRef\]](#)
- Kuşcu, İ. Skarns and skarn deposits of Turkey. In *Mineral Resources of Turkey*; Pirajno, F., Ünlü, T., Dönmez, C., Şahin, M.B., Eds.; Modern Approaches in Solid Earth Sciences; Springer: Berlin/Heidelberg, Germany, 2019; Volume 16, pp. 283–336.
- Aslan, Z.; Demir, H.; Altın, İ. U–Pb zircon geochronology and petrology of the early Miocene Göloba and Şaroluk plutons in the Biga Peninsula, NW Turkey: Implications for post-collisional magmatism and geodynamic evolution. *J. Afr. Earth Sci.* **2020**, *172*, 103998. [\[CrossRef\]](#)
- Altın, İ. Şaroluk (Gönen-Balıkesir) Granitoidinin Petrografik, Jeokimyasal ve Petrolojik Özellikleri. Master's Thesis, Balıkesir Üniversitesi Fen Bilimleri Enstitüsü, Balıkesir, Turkey, 2019.
- Aysal, N.; Ustaomer, T.; Ongen, S.; Keskin, M.; Koksall, S.; Peytcheva, I.; Fanning, M. Origin of the Early-Middle Devonian magmatism in the Sakarya Zone, NW Turkey: Geochronology, geochemistry and isotope systematics. *J. Asian Earth Sci.* **2012**, *45*, 201–222.
- Aysal, N. Petrology of the Mesozoic–Tertiary Magmatism and Metamorphism in Northern Biga (Çanakkale). Ph.D. Thesis, Istanbul University, Institute of Sciences, Istanbul, Türkiye, 2005.
- Duru, M.; Pehlivan, S.; Dönmez, M.; Ilgar, A.; Akçay, A. *Geological Map of The Balıkesir-İ18 Quadrangle*; General Directorate of Mineral Research and Exploration Ankara: Ankara, Turkey, 2007.
- Yigit, O. A prospective sector in the Tethyan Metallogenic Belt: Geology and geochronology of mineral deposits in the Biga Peninsula, NW Turkey. *Ore Geol. Rev.* **2012**, *46*, 118–148.
- Beccaleto, L. *Geology, Correlations, and Geodynamic Evolution of the Biga Peninsula (NW Turkey)*; Université de Lausanne: Lausanne, Switzerland, 2003.
- Okay, A.I.; Satir, M. Coeval plutonism and metamorphism in a latest Oligocene metamorphic core complex in northwest Turkey. *Geol. Mag.* **2000**, *137*, 495–516. [\[CrossRef\]](#)
- Özden, S.; Över, S.; Poyraz, S.A.; Güneş, Y.; Pinar, A. Tectonic implications of the 2017 Ayvacık (Çanakkale) earthquakes, Biga Peninsula, NW Turkey. *J. Asian Earth Sci.* **2018**, *154*, 125–141. [\[CrossRef\]](#)
- Okay, A.; Siyako, M.; Burkan, K. Geology and tectonic evolution of the Biga Peninsula, northwest Turkey. *Bull.-Technol. Univ. İstnab.* **1991**, *44*, 191–256.
- Yiğitbaş, E.; Tunc, İ. Pre-cambrian metamorphic rocks of the Sakarya Zone in the Biga Peninsula; late Ediacaran Gondwanaland active continental margin. *Turk. Jeol. Bul.-Geol. Bull. Turk.* **2020**, *63*, 277–302.
- Yiğitbaş, E.; Tunc, İ.; Sengun, F. Some Major Geological Problems in the Biga Peninsula: The Cetmi Melange. In Proceedings of the EGU General Assembly Conference Abstracts, Vienna, Austria, 19–24 April 2009; p. 2468.
- Şengün, F.; Yiğitbaş, E.; Tunc, İ.O. Geology and tectonic emplacement of eclogite and blueschists, Biga peninsula, northwest Turkey. *Turk. J. Earth Sci.* **2011**, *20*, 273–285. [\[CrossRef\]](#)
- Bonev, N.; Beccaleto, L.; Robyr, M.; Monié, P. Metamorphic and age constraints on the Alakeçi shear zone: Implications for the extensional exhumation history of the northern Kazdağ Massif, NW Turkey. *Lithos* **2009**, *113*, 331–345. [\[CrossRef\]](#)

20. Okay, A.; Satir, M.; Siebel, W. Pre-Alpide Palaeozoic and Mesozoic orogenic events in the Eastern Mediterranean region. *Geol. Soc. Lond. Mem.* **2006**, *32*, 389–405.
21. Afridi, B.Z. Sedimentology, Cyclostratigraphy, Sequence Stratigraphy and Geochemistry of the Middle Eocene Lacustrine-Marine Oil-Shales Transition, Mudurnu Göynük basin, NW Anatolia, Turkey. Ph.D. Thesis, Graduate School of Natural and Applied Sciences. Geological Engineering, Middle East Technical University, Ankara, Turkey, 2019.
22. Gönçüoğlu, M.C. *Introduction to the Geology of Turkey: Geodynamic Evolution of the Pre-Alpine and Alpine Terranes*; Ankara, Turkey; ODTU Jeoloji Müh. Bölümü: Ankara, Turkey, 2010; pp. 1–66.
23. Seyitoğlu, G.; Scott, B.C. The cause of N-S extensional tectonics in western Turkey: Tectonic escape vs back-arc spreading vs orogenic collapse. *J. Geodyn.* **1996**, *22*, 145–153. [\[CrossRef\]](#)
24. Dilek, Y.; Altunkaynak, Ş. Cenozoic crustal evolution and mantle dynamics of post-collisional magmatism in western Anatolia. *Int. Geol. Rev.* **2007**, *49*, 431–453.
25. Jolivet, L.; Brun, J.-P. Cenozoic geodynamic evolution of the Aegean. *Int. J. Earth Sci.* **2010**, *99*, 109–138.
26. Le Pichon, X.; Angelier, J. The Aegean Sea. Philosophical Transactions of the Royal Society of London. *Ser. A Math. Phys. Sci.* **1981**, *300*, 357–372.
27. Buick, I. The late Alpine evolution of an extensional shear zone, Naxos, Greece. *J. Geol. Soc.* **1991**, *148*, 93–103. [\[CrossRef\]](#)
28. Birkle, P.; Satir, M.; Erler, A.; Ercan, T.; Bingöl, E.; Orcen, S. Dating, geochemistry and geodynamic significance of the Tertiary magmatism of the Biga Peninsula, NW Turkey. In *Geology of the Black Sea Region: Ankara, Turkey*; Erler, A., Ed.; Mineral Research and Exploration Institute of Turkey (MTA): Ankara, Turkey, 1995; pp. 171–180.
29. Yılmaz, Y.; Genç, Ş.; Karacık, Z.; Altunkaynak, Ş. Two contrasting magmatic associations of NW Anatolia and their tectonic significance. *J. Geodyn.* **2001**, *31*, 243–271.
30. Özdamar, Ş.; Roden, M.F.; Zou, H.; Billor, M.Z.; Hames, W.; Georgiev, S.; Dunkl, I. Petrogenesis of oligocene plutonic rocks in western Anatolia (NW Turkey): Insights from mineral and rock chemistry, Sr-Nd isotopes, and U-Pb, Ar-Ar and (U-Th)/He geochronology. *Geochemistry* **2021**, *81*, 125747. [\[CrossRef\]](#)
31. Özdamar, Ş.; Zou, H.; Billor, M.Z.; Hames, W.E. Petrogenesis of mafic microgranular enclaves (MMEs) in the oligocene-miocene granitoid plutons from northwest Anatolia, Turkey. *Geochemistry* **2021**, *81*, 125713.
32. Abdelnasser, A.; Kumral, M.; Zoheir, B.; Yılmaz, H. Evolution of the Tepeoba porphyry-skarn Cu-Mo-Au deposit, NW Turkey: New mineralogical and geochemical findings. *Ore Geol. Rev.* **2022**, *147*, 104967. [\[CrossRef\]](#)
33. Karaman, M.; Kumral, M.; Yildirim, D.K.; Doner, Z.; Afzal, P.; Abdelnasser, A. Delineation of the porphyry-skarn mineralized zones (NW Turkey) using concentration–volume fractal model. *Geochemistry* **2021**, *4*, 125802. [\[CrossRef\]](#)
34. Altunkaynak, Ş.; Genç, Ş.C. Petrogenesis and time-progressive evolution of the Cenozoic continental volcanism in the Biga Peninsula, NW Anatolia (Turkey). *Lithos* **2008**, *102*, 316–340. [\[CrossRef\]](#)
35. Genç, Ş.; Altunkaynak, Ş. On the Eybek granite (Biga Peninsula, NW Anatolia): A new evaluation in the light of new geochemical data. *J. Earth Sci. Appl. Res. Cent. Hacett. Univ.* **2007**, *28*, 75–98.
36. Yılmaz, Y.; Karacık, Z. Geology of the northern side of the Gulf of Edremit and its tectonic significance for the development of the Aegean grabens. *Geodin. Acta* **2001**, *14*, 31–43. [\[CrossRef\]](#)
37. Yigit, O. Mineral deposits of Turkey in relation to Tethyan metallogeny: Implications for future mineral exploration. *Econ. Geol.* **2009**, *104*, 19–51. [\[CrossRef\]](#)
38. Carr, M. *Igpet 2007 for Windows XP or Vista*; Terra Softa Inc.: Somerset, NJ, USA, 2007.
39. Coelho, J. GEOISO—A Windows™ program to calculate and plot mass balances and volume changes occurring in a wide variety of geologic processes. *Comput. Geosci.* **2006**, *32*, 1523–1528. [\[CrossRef\]](#)
40. Grant, J.A. Isocon analysis: A brief review of the method and applications. *Phys. Chem. Earth Parts A/B/C* **2005**, *30*, 997–1004. [\[CrossRef\]](#)
41. Gresens, R.L. Composition-volume relationships of metasomatism. *Chem. Geol.* **1967**, *2*, 47–65. [\[CrossRef\]](#)
42. Armstrong, J.T. Citzaf—a package of correction programs for the quantitative Electron Microbeam X-ray-Analysis of thick polished materials, thin-films, and particles. *Microbeam Anal.* **1995**, *4*, 177–200.
43. Krushensky, R.; Akcay, Y.; Karaege, E. *Geology of the Karalar-Yesiler Area, Northwest Anatolia, Turkey*; 2331-1258; US Geological Survey: Tallahassee, FL, USA, 1974.
44. Bingöl, E.; Akyürek, B.; Korkmaz, B. Geology of the Biga Peninsula and some characteristics of the Karakaya Formation. In Proceedings of the 50th Anniversary of Turkish Republic Earth Science Congress Ankara, Ankara, Turkey, 17–19 December 1973; pp. 70–77.
45. Krushensky, R. Neogene calc-alkaline extrusive and intrusive rocks of the karalar-yesiller area: Northwest Anatolia, Turkey. *Bull. Volcanol.* **1975**, *39*, 336–360.
46. Okay, A.I.; Gönçüoğlu, M.C. The Karakaya Complex: A review of data and concepts. *Turk. J. Earth Sci.* **2004**, *13*, 75–95.
47. Dönmez, M.; Akçay, A.E.; Genç, Ş.C.; Şükrü, A. Middle-late Eocene volcanism and marine ignimbrites in Biga peninsula (NW Anatolia-Turkey). *Bull. Miner. Res. Explor.* **2005**, *131*, 21.
48. Karacık, Z.; Yılmaz, Y.; Pearce, J.A. The Dikili-Çandarlı volcanics, Western Turkey: Magmatic interactions as recorded by petrographic and geochemical features. *Turk. J. Earth Sci.* **2007**, *16*, 493–522.
49. Middlemost, E.A. Naming materials in the magma/igneous rock system. *Earth-Sci. Rev.* **1994**, *37*, 215–224. [\[CrossRef\]](#)

50. Irvine, T.; Baragar, W. A guide to the chemical classification of the common volcanic rocks. *Can. J. Earth Sci.* **1971**, *8*, 523–548. [\[CrossRef\]](#)
51. Kuno, H. Differentiation of basalt magmas. *Basalts Poldervaart Treatise Rocks Basaltic Compos.* **1968**, *2*, 623–688.
52. Petro, W.L.; Vogel, T.A.; Wilband, J.T. Major-element chemistry of plutonic rock suites from compressional and extensional plate boundaries. *Chem. Geol.* **1979**, *26*, 217–235.
53. Shand, S. On the relations between silica, alumina, and the bases in eruptive rocks, considered as a means of classification. *Geol. Mag.* **1927**, *64*, 446–449. [\[CrossRef\]](#)
54. Ishihara, S. The magnetite-series and ilmenite-series granitic rocks. *Min. Geol.* **1977**, *27*, 293–305.
55. Sun, S.-S.; McDonough, W. Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. *Geol. Soc. Lond. Spec. Publ.* **1989**, *42*, 313–345. [\[CrossRef\]](#)
56. Miyashiro, A.; Shido, F. Tholeiitic and calc-alkalic series in relation to the behaviors of titanium, vanadium, chromium, and nickel. *Am. J. Sci.* **1975**, *275*, 265–277. [\[CrossRef\]](#)
57. Taylor, S.R.; McLennan, S.M. *The Continental Crust: Its Composition and Evolution*; Blackwell Scientific Publications: Boston, MA, USA, 1985.
58. Chappell, B.W.; White, A. I- and S-type granites in the Lachlan Fold Belt. *Earth Environ. Sci. Trans. R. Soc. Edinb.* **1992**, *83*, 1–26.
59. Chappell, B.W.; White, A.J.R. Two contrasting granite types: 25 years later. *Aust. J. Earth Sci.* **2001**, *48*, 489–499. [\[CrossRef\]](#)
60. Pearce, J.A.; Harris, N.B.; Tindle, A.G. Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. *J. Petrol.* **1984**, *25*, 956–983. [\[CrossRef\]](#)
61. Pearce, J. Sources and settings of granitic rocks. *Epis. J. Int. Geosci.* **1996**, *19*, 120–125. [\[CrossRef\]](#)
62. Floyd, P.; Leveridge, B. Tectonic environment of the Devonian Gramscatho basin, south Cornwall: Framework mode and geochemical evidence from turbiditic sandstones. *J. Geol. Soc.* **1987**, *144*, 531–542.
63. Roser, B.; Korsch, R. Determination of tectonic setting of sandstone-mudstone suites using content and ratio. *J. Geol.* **1986**, *5*, 635–650. [\[CrossRef\]](#)
64. Condie, K.C.; Macke, J.E.; Reimer, T.O. Petrology and geochemistry of early Precambrian graywackes from the Fig Tree Group, South Africa. *Geol. Soc. Am. Bull.* **1970**, *81*, 2759–2776. [\[CrossRef\]](#)
65. van de Kamp, P.C.; Leake, B.E.; Senior, A. The petrography and geochemistry of some Californian arkoses with application to identifying gneisses of metasedimentary origin. *J. Geol.* **1976**, *84*, 195–212. [\[CrossRef\]](#)
66. Caby, R.; Dostal, J.; Dupuy, C. Upper Proterozoic volcanic graywackes from northwestern Hoggar (Algeria)—Geology and geochemistry. *Precambrian Res.* **1977**, *5*, 283–297.
67. van de Kamp, P.C. Geochemistry and origin of metasediments in the Haliburton-Madoc area, southeastern Ontario. *Can. J. Earth Sci.* **1968**, *5*, 1337–1372. [\[CrossRef\]](#)
68. Milani, L.; Lehmann, J.; Naydenov, K.V.; Saalman, K.; Nex, P.A.; Kinnaird, J.A.; Friedman, I.S.; Woolrych, T.; Selley, D. Geology and mineralization of the Cu-rich Mumbwa district, a potential IOCG-type system at the eastern margin of the Pan-African Hook batholith, Zambia. *J. Afr. Earth Sci.* **2019**, *158*, 103513.
69. Ishikawa, Y.; Sawaguchi, T.; Iwaya, S.; Horiuchi, M. Delineation of prospecting targets for Kuroko deposits based on modes of volcanism of underlying dacite and alteration halos. *Min. Geol.* **1976**, *26*, 105–117.
70. Williams, N.C.; Davidson, G.J. Possible submarine advanced argillic alteration at the Basin Lake prospect, Western Tasmania, Australia. *Econ. Geol.* **2004**, *99*, 987–1002.
71. Bonnet, A.-L.; Corriveau, L. Alteration vectors to metamorphosed hydrothermal systems in gneissic terranes. In *Mineral Deposits of Canada: A Synthesis of Major Deposit-Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods*; Goodfellow, W., Ed.; Geological Association of Canada, Mineral Deposits Division, Special Publication: St. John's, NL, Canada, 2007; Volume 5, pp. 1035–1049.
72. Bonnet, A.-L.; Corriveau, L.; La Flèche, M.R. Chemical imprint of highly metamorphosed volcanic-hosted hydrothermal alterations in the La Romaine Supracrustal Belt, eastern Grenville Province, Quebec. *Can. J. Earth Sci.* **2005**, *42*, 1783–1814.
73. Mange, M.A.; Morton, A.C. Chapter 13 Geochemistry of Heavy Minerals. In *Developments in Sedimentology*; Mange, M.A., Wright, D.T., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Volume 58, pp. 345–391.
74. Morimoto, N. Die Nomenklatur von Pyroxenen. *Mineral. Petrol.* **1988**, *39*, 55–76. [\[CrossRef\]](#)
75. Deer, W.A.; Howie, R.A.; Zussman, J. *An Introduction to the Rock-forming Minerals-Second Edition*; Mineralogical Society of Great Britain and Ireland: Middlesex, UK, 1992; p. 696.
76. Yavuz, F.; Yıldırım, D.K. A Windows program for calculation and classification of epidote–supergroup minerals. *Periodico di Mineralogia* **2018**, *87*, 228–269.
77. Tischendorf, G.; Gottesmann, B.; Förster, H.-J.; Trumbull, R.B. On Li-bearing micas: Estimating Li from electron microprobe analyses and an improved diagram for graphical representation. *Mineral. Mag.* **1997**, *61*, 809–834.
78. Nachit, H.; Ibhi, A.; Ohoud, M.B. Discrimination between primary magmatic biotites, reequilibrated biotites and neoformed biotites. *Comptes Rendus Geosci.* **2005**, *337*, 1415–1420.
79. Boomeri, M.; Nakashima, K.; Lentz, D.R. The Miduk porphyry Cu deposit, Kerman, Iran: A geochemical analysis of the potassic zone including halogen element systematics related to Cu mineralization processes. *J. Geochem. Explor.* **2009**, *103*, 17–29.
80. Henry, D.J.; Guidotti, C.V.; Thomson, J.A. The Ti-saturation surface for low-to-medium pressure metapelitic biotites: Implications for geothermometry and Ti-substitution mechanisms. *Am. Mineral.* **2005**, *90*, 316–328. [\[CrossRef\]](#)

81. Tindle, A.G.; Webb, P.C. Estimation of lithium contents in trioctahedral micas using microprobe data: Application to micas from granitic rocks. *Eur. J. Mineral.* **1990**, *2*, 595–610. [\[CrossRef\]](#)
82. Zane, A.; Weiss, Z. A procedure for classifying rock-forming chlorites based on microprobe data. *Rend. Lincei* **1998**, *9*, 51–56. [\[CrossRef\]](#)
83. Cathelineau, M. Cation site occupancy in chlorites and illites as function of temperature. *Clay Miner.* **1988**, *23*, 471–485.
84. Tindle, A. Chlorite Formula Unit Calculator and Variety Namer. 2010. Available online: http://www.open.ac.uk/earth-research/tindle/AGT/AGT_Home_2010/Microprobe-2.html (accessed on 20 February 2018).
85. Franz, G.; Liebscher, A. Physical and chemical properties of the epidote minerals—An Introduction. *Rev. Mineral. Geochem.* **2004**, *56*, 1–81. [\[CrossRef\]](#)
86. Nachit, H.; Razafimahefa, N.; Stussi, J.-M.; Carron, J.-P. Composition chimique des biotites et typologie magmatique des granitoides. *C. R. De L'académie Des Sci. Série 2 Mécanique Phys. Chim. Sci. L'univers Sci. Terre* **1985**, *301*, 813–818.
87. Abdel-rahman, A.-F.M. Nature of Biotites from Alkaline, Calc-alkaline, and Peraluminous Magmas. *J. Petrol.* **1994**, *35*, 525–541. [\[CrossRef\]](#)
88. Zhou, Z. The origin of intrusive mass in Fengshandong, Hubei province. *Acta Petrol. Sin.* **1986**, *2*, 59–70.
89. Leake, B.E.; Woolley, A.R.; Arps, C.E.; Birch, W.D.; Gilbert, M.C.; Grice, J.D.; Hawthorne, F.C.; Kato, A.; Kisch, H.J.; Krivovichev, V.G. Nomenclature of amphiboles; report of the subcommittee on amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. *Can. Mineral.* **1997**, *35*, 219–246.
90. Lin, S. A contribution to the chemistry, origin and evolution of magnetite. *Acta Mineral. Sin.* **1982**, *3*, 166–174.
91. Dupuis, C.; Beaudoin, G. Discriminant diagrams for iron oxide trace element fingerprinting of mineral deposit types. *Miner. Depos.* **2011**, *46*, 319–335.
92. Meyer, C.; Hemley, J.J. Wall rock alteration. *Geochem. Hydrother. Ore Depos.* **1967**, *1*, 166.
93. Kumral, M.; Abdelnasser, A.; Budakoglu, M. Geochemistry of Hydrothermal Alteration Associated with Cenozoic Intrusion-Hosted Cu-Pb-Zn Mineralization at Tavşanlı Area, Kütahya, NW Turkey. *Minerals* **2016**, *6*, 13. [\[CrossRef\]](#)
94. Middelburg, J.J.; van der Weijden, C.H.; Woittiez, J.R. Chemical processes affecting the mobility of major, minor and trace elements during weathering of granitic rocks. *Chem. Geol.* **1988**, *68*, 253–273.
95. Grant, J.A. The isocon diagram; a simple solution to Gresens' equation for metasomatic alteration. *Econ. Geol.* **1986**, *81*, 1976–1982. [\[CrossRef\]](#)
96. Babazadeh, S.; Ghalamghash, J.; D'Antonio, M.; Furman, T. Hydrothermal alteration in Eshtehard volcanoes, Iran: Constraints from trace elements redistribution and stable isotope geochemistry. *J. Geochem. Explor.* **2021**, *222*, 106719. [\[CrossRef\]](#)
97. Zarayskiy, G.P.; Zharikov, V.A.; Stoyanovskaya, F.M.; Balashov, V.N. The experimental study of bimetasomatic skarn formation. *Int. Geol. Rev.* **1987**, *29*, 761–858. [\[CrossRef\]](#)
98. Mollo, S.; Misiti, V.; Scarlato, P.; Soligo, M. The role of cooling rate in the origin of high temperature phases at the chilled margin of magmatic intrusions. *Chem. Geol.* **2012**, *322–323*, 28–46. [\[CrossRef\]](#)
99. Candela, P.; Piccoli, P. Model ore-metal partitioning from melts into vapor and vapor/brine mixtures. In *Magma, Fluids and Ore Deposits*; Thompson, J., Ed.; Mineralogical Association of Canada Short Course: Québec, QC, Canada, 1995; Volume 23, pp. 101–127.
100. Sharma, R.; Srivastava, P.K. Hydrothermal Fluids of Magmatic Origin. In *Modelling of Magmatic and Allied Processes*; Springer: Berlin/Heidelberg, Germany, 2014; pp. 181–208.
101. Mokhtari, M.A.A.; Kouhestani, H.; Gholizadeh, K. Mineral chemistry and formation conditions of calc-silicate minerals of Qozlou Fe skarn deposit, Zanjan Province, NW Iran. *Arab. J. Geosci.* **2019**, *12*, 658. [\[CrossRef\]](#)
102. Jamtveit, B.; Wogelius, R.A.; Fraser, D.G. Zonation patterns of skarn garnets: Records of hydrothermal system evolution. *Geology* **1993**, *21*, 113–116. [\[CrossRef\]](#)
103. Akiska, S. Crystallization conditions and compositional variations of silicate and sulfide minerals in the Pb-Zn skarn deposits, Biga Peninsula, NW Turkey. *Ore Geol. Rev.* **2020**, *118*, 103322. [\[CrossRef\]](#)
104. Hantsche, A.L.; Kouzmanov, K.; Milenkov, G.; Vezzoni, S.; Vassileva, R.; Dini, A.; Sheldrake, T.; Laurent, O.; Guillong, M. Metasomatism and cyclic skarn growth along lithological contacts: Physical and geochemical evidence from a distal PbZn skarn. *Lithos* **2021**, *400–401*, 106408. [\[CrossRef\]](#)
105. Zhong, S.; Feng, C.; Seltmann, R.; Dolgoplova, A.; Andersen, J.C.Ø.; Li, D.; Yu, M. Sources of fluids and metals and evolution models of skarn deposits in the Qimantagh metallogenic belt: A case study from the Weibao deposit, East Kunlun Mountains, northern Tibetan Plateau. *Ore Geol. Rev.* **2018**, *93*, 19–37. [\[CrossRef\]](#)
106. Cui, F.-H.; Zhang, C.; Jin, D.-T.; Wang, L.-Y.; Gao, J.-L.; Ma, M.; Li, Y.-D. Mineral Chemistry of the Lower Cretaceous Jinling Iron Skarn Deposit, Western Shandong Province, North China Craton: Implications for the Iron Skarn Mineralization Process. *Minerals* **2022**, *12*, 1152. [\[CrossRef\]](#)
107. Gustafson, W.I. The Stability of Andradite, Hedenbergite, and Related Minerals in the System Ca-Fe-Si-O-H. *J. Petrol.* **1974**, *15*, 455–496. [\[CrossRef\]](#)
108. Easton, A.; Hamilton, D.; Kempe, D.; Sheppard, S. Low-temperature metasomatic garnets in marine sediments. *Philos. Trans. R. Soc. Lond. Ser. A Math. Phys. Sci.* **1977**, *286*, 253–271.
109. Rajabpour, S.; Hassanpour, S.; Jiang, S.-Y. Physicochemical evolution and mechanism of a skarn system: Insights from the world-class Mazraeh Cu deposit, NW Iran. *GSA Bull.* **2023**, published online.

110. Öztürk, Y.Y. *Mineralogic and Petrographic Investigation of Skarn Alteration Zones Related to the Evciler Granitoid, Kazdağ Northwestern Anatolia*; DEÜ Fen Bilimleri Enstitüsü: Buca/İzmir, Türkiye, 2006.
111. Pan, Y.; Lentz, D. Scapolite in skarn deposits: Petrogenetic and geochemical significance. *Miner. Intrusion-Relat. Skarn Syst. Mineral. Assoc. Can. Short Course Ser.* **1998**, *26*, 169–209.
112. Jiang, J.; Gao, S.; Zheng, Y.; Lentz, D.R.; Huang, J.; Liu, J.; Tian, K.; Jiang, X. Geological, Geochemical, and Mineralogical Constraints on the Genesis of the Polymetallic Pb-Zn-Rich Nuocang Skarn Deposit, Western Gangdese, Tibet. *Minerals* **2020**, *10*, 839. [\[CrossRef\]](#)
113. Xie, H.; Huang, X.; Meng, Y.; Tan, H.; Qi, L. Discrimination of Mineralization Types of Skarn Deposits by Magnetite Chemistry. *Minerals* **2022**, *12*, 608. [\[CrossRef\]](#)
114. Einaudi, M.; Meinert, L.; Newberry, R. Skarn Deposits. *Econ. Geol.* **1981**, *1905–1980*, 317–391.
115. Meinert, L.D. Compositional variation of igneous rocks associated with skarn deposits—chemical evidence for a genetic connection between petrogenesis and mineralization. *Mineral. Assoc. Can. Short Course Ser.* **1995**, *23*, 401–418.
116. Smirnov, V.I.; Dunham, K.C.; Creighton, H. *Geology of Mineral Deposits*; MIR Publishers: Moscow, Russia, 1976; p. 520.
117. Uchida, E.; Iiyama, J.T. Physicochemical study of skarn formation in the Shinyama iron-copper ore deposit of the Kamaishi mine, northeastern Japan. *Econ. Geol.* **1982**, *77*, 809–822. [\[CrossRef\]](#)
118. Meinert, L.D. Mineralogy and petrology of iron skarns in western British Columbia, Canada. *Econ. Geol.* **1984**, *79*, 869–882. [\[CrossRef\]](#)
119. Oyman, T. Geochemistry, mineralogy and genesis of the Ayazmant Fe–Cu skarn deposit in Ayvalık, (Balıkesir), Turkey. *Ore Geol. Rev.* **2010**, *37*, 175–201. [\[CrossRef\]](#)
120. Mollai, H.; Pe-Piper, G.; Dabiri, R. Genetic relationships between skarn ore deposits and magmatic activity in the Ahar region, Western Alborz, NW Iran. *Geol. Carpathica* **2014**, *65*, 209–227. [\[CrossRef\]](#)
121. Einaudi, M.T.; Burt, D.M. Introduction; terminology, classification, and composition of skarn deposits. *Econ. Geol.* **1982**, *77*, 745–754. [\[CrossRef\]](#)
122. Öztürk, Y.Y.; Helvacı, C. Skarn alteration and Au–Cu mineralization associated with Tertiary granitoids in northwestern Turkey: Evidence from the Evciler deposit, Kazdağ Massif, Turkey. *Econ. Geol.* **2008**, *103*, 1665–1682. [\[CrossRef\]](#)
123. Öztürk, Y.Y.; Helvacı, C.; Satır, M. Genetic relations between skarn mineralization and petrogenesis of the Evciler Granitoid, Kazdağ, Çanakkale, Turkey and comparison with world skarn granitoids. *Turk. J. Earth Sci.* **2005**, *14*, 255–280.
124. Karaaslan, N.; Başarı, N. Geological report on Balıkesir–Edremit–Yaşyer (Yalaktepe) Fe mineralization. *MTA Rep.* **1979**, 6612.
125. Gümüş, A. *Contribution à l'étude Géologique du Secteur Septentrional de Kalabak Köy-Eymir Köy (Région d'Edremit) Turquie*; Maden Tetkik ve Arama Enstitüsü: Dar es Salaam, Tanzania, 1964.
126. Dora, O. The mineralogical investigation of the Fe–Zn–S system in connection with contact-metasomatic and hydrothermal sphalerite deposits. In *Scientific Reports of the Faculty of Science, Ege University*; Ege University: Izmir, Turkey, 1971.
127. Önal, G.; Yüce, A.; Boylu, F.; Tarkan, M.; Fişne, A.; Kökçüoğlu, O.; Avcıoğlu, N.; Kur, M.; Binici, P.; Karaoğlu, M. *General and Economic Geology of Biga Peninsula*; MTA Report No. 11101; Mineral Research and Exploration Institute of Turkey: Ankara, Turkey, 2009.
128. Tamer, Y.; Kurt, M. *Feasibility Report on Balıkesir–Şamlı-Bakırlık Tepe Fe Mineralization*; MTA Report No. 1835; Mineral Research and Exploration Institute of Turkey: Ankara, Turkey, 1982.
129. Öztürk, Y.Y.; Helvacı, C.; Satır, M. The influence of meteoric water on skarn formation and late-stage hydrothermal alteration at the Evciler skarn occurrences, Kazdağ, NW Turkey. *Ore Geol. Rev.* **2008**, *34*, 271–284. [\[CrossRef\]](#)
130. Gjelsvik, T. Kuzeybatı Anadolu Kurşun–Çinko Zuhurlarında Yapılan Araştırmalar. *Bull. Miner. Res. Explor.* **1962**, *59*, 60–68.
131. Arik, F.; Aydın, U. Mineralogical and petrographical characteristics of the Aladag skarn deposit (Ezine/Çanakkale–West Turkey). *Sci. Res. Essays* **2011**, *6*, 592–606.
132. Öngen, S.; Aysal, N.; Azaz, D. Geochemical and mineralogical relationships between manganese silicate minerals and zinc ore mineralization at Gürece contact aureole (Biga Peninsula, NW-Turkey). *İstanbul Yerbilim. Derg.* **2012**, *25*, 85–103.
133. Mesut, A. Yenice (Arapuçandere–Kurttaş–Sofular ve Kalkım Handeresi) Pb–Zn–Cu Cevherleşmelerinin Köken Sorunu ve Tersiyer Volkanizmasıyla ilişkileri. *Jeol. Mühendisliği Derg.* **1984**, *8*, 19–30.
134. Tufan, E. Geology, paragenesis and formation of the Pb–Zn occurrence of Karaaydın village (Yenice–Çanakkale). *Niğde Univ. J. Eng. Sci.* **2003**, *7*, 95–106.
135. Yücelay, M. *Geological Report on the Karaaydın (Kalkım–Yenice–Çanakkale) Pb Mineralization, Çanakkale*; MTA Report No. 229; Mineral Research and Exploration Institute of Turkey: Ankara, Turkey, 1975.
136. Mollai, H. Petrochemistry and Genesis of the Granodiorite and Associated Iron–Copper Skarn Deposit of Mazraeh, Ahar, East Azarbaijan. Iran. Ph.D. Thesis, University of Roorkee, Roorkee, India, 1993, unpublished.

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