

Article

Origin of Talc and Fe-Ti-V Mineralization in the Kletno Deposit (the Śnieżnik Massif, SW Poland)

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Abstract: The Kletno deposit in the Śnieżnik Massif (Central Sudetes, SW Poland), mined for Fe, U, Ag, Cu, fluorite, and marble through the ages, developed at the contact of marbles and orthogneiss. Here, we present a new Fe-Ti-V-ore (containing up to 14.07 wt. % Fe, 2.05 wt. % Ti, and 2055 ppm V in bulk rock) and ornamental- to gem-quality talc prospect at the southwest margin of this deposit. This newly documented Fe-Ti-V mineralization is hosted in hornblendites, dolomite veins, and chlorite schists, which, along with talc, envelopes a tectonic slice of serpentinite. Hornblendites are interpreted as metamorphosed ferrogabbros, derived from the same mafic melts as adjacent barren metagabbros. The oxygen and carbon isotope compositions of metabasites and dolomite veins (amphibole $\delta^{18}\text{O}$ values = 8.8–9.3‰; carbonate $\delta^{18}\text{O}$ values = 12.8–16.0‰, and $\delta^{13}\text{C}$ values = −8.3‰ to −7.2‰), in combination with those of the country marbles (carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values = 23.2‰ and +0.1‰, respectively), suggest that mineralization-bearing hornblendites formed due to interaction of the mafic magma with CO_2 released during the decarbonation of the sediments. The CO_2 -bearing fluid interaction with gabbros likely caused carbonation of the gabbros and formation of the dolomite veins, whereas talc formed due to Si-rich fluids, possibly derived from a mafic intrusion, interaction with serpentinite, or due to the metasomatism of the serpentinite–gabbro assemblage. Moreover, fluids leaching Fe and Ti from the adjacent sediments can mix with the mafic magma causing enrichment of the magma in Fe and Ti. Consequently, the mineralization-bearing ferrogabbros became even more enriched in Fe and Ti, which can be linked with the formation of Fe-Ti-V ore bodies.

Keywords: Śnieżnik Massif; Kletno deposit; Fe-Ti-V mineralization; talc; carbonate veins; stable isotopes; serpentinite-gabbro-sediment assemblage

1. Introduction

The Kletno deposit, located in the Kleśnica valley in the Śnieżnik Massif (Central Sudetes, SW Poland), was subject to long-lasting underground and open-pit mining, which began in the 13th to 14th centuries and ceased in the 1990s [1]. The cessation of mining was due to the discovery of a famous cave system in 1966, known as the Jaskinia Niedźwiedzia (the Bear Cave) (e.g., Kasprzak et al. [2]). The Kletno deposit was mined for Fe, U, Ag, and Cu ores, as well as fluorite and the famous Biała Marianna marble [1].

Kletno is a polymetallic deposit, in which mineralization is associated with skarns [3,4]. Due to deposit's good accessibility, the skarn mineralization at the contact of marbles, schists, and paragneisses of the Stronie sequence with the Śnieżnik orthogneiss is relatively well-studied. However, poorer studied mineralized zones are present farther southwest, near the culmination of the Żmijowiec Rib, where serpentinite and metabasite bodies are enclosed within the Stronie sequence metasediments. The best described unit is the serpentinite body, which has been the subject of several studies concerning its position against the country rocks, petrological and geochemical characteristics, and a description of the soil and vegetation associated [5–12]. However, the metabasites and dolomite veins penetrating the serpentinite lack a detailed study of ore mineralization, which differs from that known from the major parts of the Kletno deposit in the Kleśnica valley. The unusual, Fe-Ti-V mineralization-bearing dolomite veins, despite their temporal and genetic association with altered ultrabasites, cannot be termed as listvenites because they are devoid of fuchsite and quartz [13].

This manuscript describes the mineralization related to serpentinite and metabasites from the Żmijowiec Rib at the southwestern margin of the Kletno deposit and focuses on the new observation of Fe-Ti-V mineralization and ornamental- to gem-quality talc in this deposit. A new model of joint Fe-Ti-V mineralization, and talc and dolomite veins formation, is proposed, allowing for reinterpretation of the tectonic model for the area.

2. Geological Setting and Description of the Deposit

The Kletno deposit is located in the Śnieżnik Massif, which makes up the eastern limb of the Orlica-Śnieżnik Dome (OSD), located at the NE margin of the Bohemian Massif (Figure 1) of the European Variscides. The Orlica-Śnieżnik Dome belongs to the Central Sudetes, interpreted as an accretionary wedge, which is located between the Saxo-Thuringia (Cadomia) and Brunia (Avalonia) terranes [14]. In the Central Sudetes, various basic and ultrabasic rocks are widespread, albeit that the largest masses of these form the Central-Sudetic Ophiolite and are interpreted as ca. 400 Ma remnants of the Rheic Ocean, obducted during the Variscan Orogeny [15–17]. Metabasites of the Ślęza Ophiolite, being the largest segment of the Central-Sudetic Ophiolite, host the well-studied magmatic Fe-Ti-V deposit [17].

The oldest segment of the Orlica-Śnieżnik Dome is the supracrustal succession known as the Młynowiec-Stronie Group [18]. In the Śnieżnik Massif, the Młynowiec-Stronie Group is subdivided into: 1) the Młynowiec paragneiss, containing minor mica schist and amphibolite, and 2) the Stronie sequence, composed of mica schist and subordinate paragneiss, quartzite, graphite schist, calcic and dolomitic marbles, amphibolite, and felsic metavolcanics [19]. Near Kletno, these marbles were affected by polyphase deformation at low- to medium-grade metamorphism conditions (peak temperature ~500°C based on Mg content in calcite) (see Jastrzębski [20], and references therein). Metabasites from the western wing of the OSD are interpreted as enriched mid-ocean ridge basalt (E-MORB) and normal mid-ocean ridge basalt-like (N-MORB-like), as well as depleted tholeiitic diabases, basalts and pillow basalts, and subordinate ocean-island basalt-like (OIB-like) alkaline diabases, which are all coeval with sedimentation of the Stronie sequence protolith [21]. The maximum sedimentation age of the Stronie sequence, based on detrital zircons, is estimated to be 532 ± 6 Ma, whereas that of the underlying Młynowiec paragneiss is 563 ± 6 Ma [19].

The Młynowiec-Stronie Group was intruded by large volumes of ca. 500 Ma granites during a magmatic event widespread across Variscan terranes [22]. In the OSD, these granites are transformed into the Śnieżnik and Gierałtów orthogneisses [23], constituting the majority of the OSD. The OSD rocks underwent pervasive polyphase deformation and metamorphism ca. 340 Ma [24]. This tectonothermal event is also related to migmatization as evidenced by the SHRIMP age of 342 ± 6 Ma of the rims of zoned zircon grains from the Gierałtów and Śnieżnik orthogneisses [23].

The Skrzynka Shear Zone at the northern margin of the Śnieżnik Massif hosts the Złoty Stok deposit, known for its economic concentrations of Au, As, Fe, Pb, and U, as well as W mineralization and nephrite occurrence [25–33]. Mineralization in the Złoty Stok deposit developed at the contact of marble bodies with the composite, syn-collisional Kłodzko-Złoty Stok granitic pluton, emplaced at ca. 350–330 Ma [29,34–36]. In addition, small granitic veins called the Jawornik granitoids, dated to similar age span of ca. 350–340 Ma,

intruded the Skrzynka Shear Zone [37,38]. However, the northwestern-most zones of the Kłodzko-Złoty Stok pluton are related with the post-tectonic magmatic activity ca. 300 Ma [36], associated with the initiation of the Permo-Mesozoic lithospheric thinning [39]. Additionally, ca. 330 Ma Kudowa-Oleśnice granitoids intruded the NW margin of the OSD [35,40] and post-tectonic, 326 ± 3 Ma syenite dykes cut the Gierałtów-Śnieżnik orthogneiss of the western wing of the OSD [41].

A few kilometers east of the Kletno deposit, the Orlica-Śnieżnik Dome borders with the Staré Město Belt, which is a boundary of the Central and East Sudetes. The Staré Město Belt is composed of high-grade metasediments, banded felsic rocks, amphibolites, sheared gabbros, and spinel peridotites, and is cut by a syn-tectonic ~340 Ma tonalite intrusion [42,43].

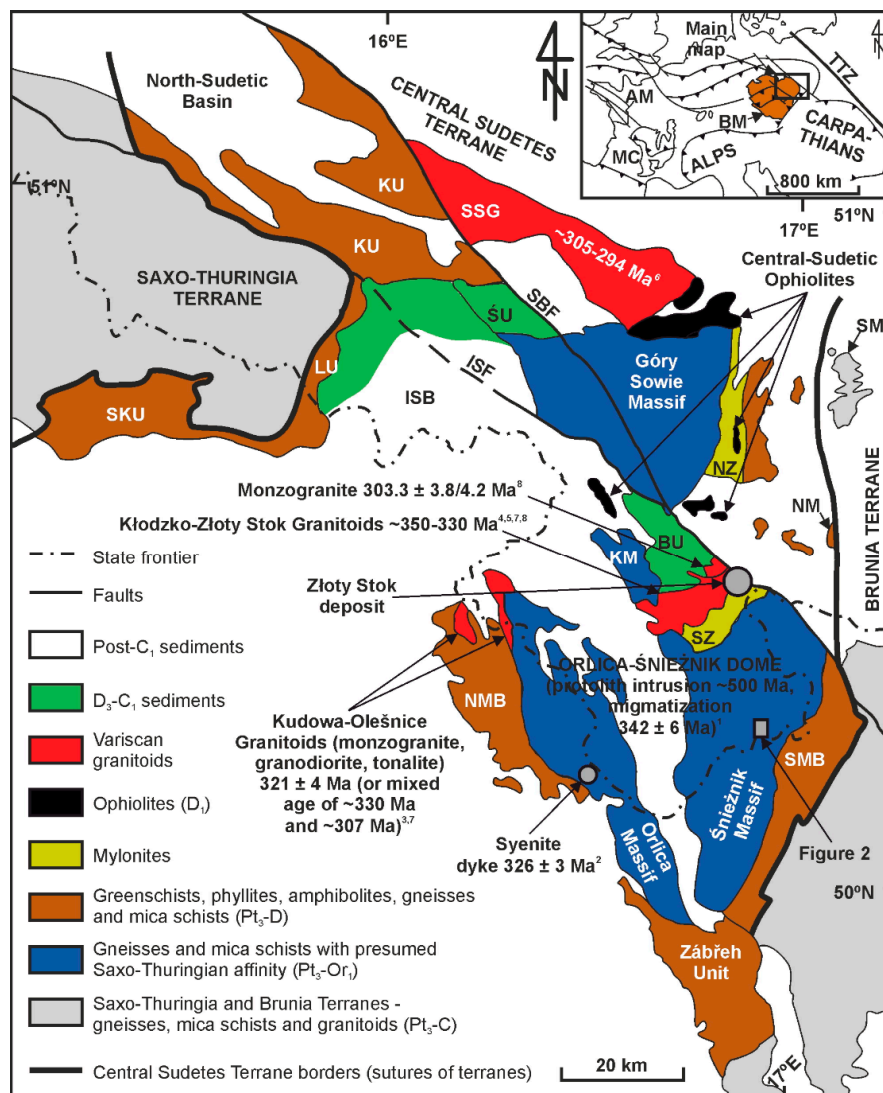


Figure 1. Geological map of the Central Sudetes (modified after Mazur et al. [14]); the inset map shows their location in Europe (modified after Mazur et al. [43]). Ages are from: 1—Turniak et al. [23], 2—Żelaźniewicz et al. [41], 3—Mikulski et al. [40], 4—Mikulski et al. [29], 5—Mikulski and Williams [34], 6—Turniak et al. [39], 7—Oberc-Dziedzic et al. [35], and 8—Jokubauskas et al. [36]. Abbreviations: AM—Armorican Massif, BM—Bohemian Massif, BU—Bardo Sedimentary Unit, ISB—Intra-Sudetic Basin, ISF—Intra-Sudetic Fault, KM—Kłodzko Massif, KU—Kaczawa Unit, LU—Leszczyniec Unit, MC—Massif Central, NM—Niedźwiedz Massif, NMB—Nové Město Belt, NZ—Niemcza Shear Zone, SBF—Sudetic Boundary Fault, SKU—South Karkonosze Unit, SM—Strzelin Massif, SMB—Staré Město Belt, SSG—Strzegom-Sobótka Granite, SZ—Skrzynka Shear Zone, ŚU—Świebodzice Sedimentary Unit, TTZ—Tessieyre-Tornquist Zone.

The area of past mining in the Kleśnica valley in Kletno is situated at the eastern contact of the Stronie sequence metasediments with the Śnieżnik Orthogneiss in the area in which numerous marble bodies are present (Figure 2). The calcite Biała Marianna marble sample, examined in this study as an example of carbonate wall-rock, is from the abandoned quarry in this area. In addition, subordinate quartzite bodies, as well as quartz veins cutting the metasediments, are present in the area of past mining [8,9]. Several ore minerals have been documented in this section of the Kletno deposit including: magnetite, hematite (martite), cassiterite, uraninite, fourmarierite ($\text{Pb}(\text{UO}_2)_4\text{O}_3(\text{OH})_4 \cdot 4(\text{H}_2\text{O})$), pyrite, pyrrhotite, chalcopyrite, bornite, chalcocite, covellite, cosalite, galena, cinnabar, stromeyerite (AgCuS), wittichenite (Cu_3BiS_3), sphalerite (including high-Fe sphalerite), arsenopyrite, tetrahedrite, miargyrite (AgSbS_2), clausthalite (PbSe), umangite (Cu_3Se_2), klockmannite (CuSe), tiemannite (HgSe), naumannite (Ag_2Se), bohdanowiczite (AgBiSe_2), eskebornite (CuFeSe_2), malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$), azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), cerussite (PbCO_3), metatorbernite ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$), autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 11(\text{H}_2\text{O})$), anglesite (PbSO_4), barite, chrysocolla ($((\text{Cu},\text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n(\text{H}_2\text{O}))$), uranophane ($\text{Ca}(\text{UO}_2)_2\text{SiO}_3(\text{OH})_2 \cdot 5(\text{H}_2\text{O})$), titanite, fluorite, gold and silver (native elements), and graphite [3,4].

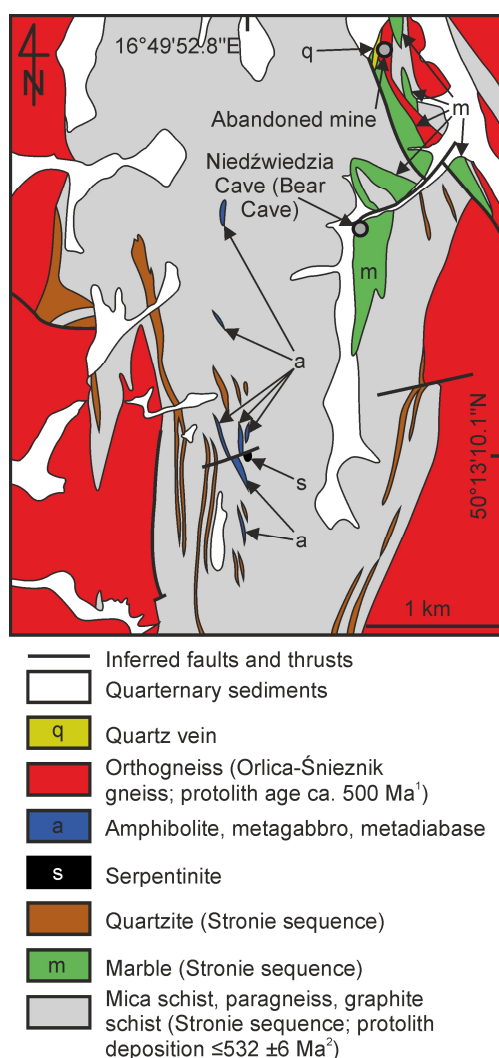


Figure 2. Schematic geological map of the Kletno deposit and Żmijowiec Rib (modified after Frąckiewicz and Teisseyre [8]). Ages are from: 1—Turniak et al. [23], 2—Mazur et al. [19]. Abbreviations: a—amphibolite, metagabbro, metadiabase, m—marble of the Stronie sequence, q—quartz vein, s—serpentine.

About 1.5 km southwest from the best-recognized sections of the Kletno deposit and a few hundred meters from the western contact with the Śnieżnik Orthogneiss, a single serpentinite body and several elongated amphibolite, metagabbro and metadiabase bodies (resembling displaced veins), are embedded in the Stronie succession (Figure 2). This part of the Stronie sequence is composed of paragneiss and mica schist, in which quartzite (including graphite quartzite) intercalations are common. The serpentinite from Kletno was previously interpreted as a peridotite melt or crystal mush, which intruded the metasediments in the form of a vein, or an already-serpentinized peridotite, which was in the semi-solid state tectonically emplaced between metasedimentary layers [5–10].

3. Materials and Methods

Structural measurements (Table S1) were processed in the Stereonet software (version 10.2.8, Cornell University, Ithaca, NY, USA) by Richard W. Allmendinger, using algorithms of Allmendinger et al. [44] and Cardozo and Allmendinger [45]. Samples of serpentinite, talc schist, barren metagabbro and metadiabase, Fe-Ti-V-mineralized hornblendite, dolomite vein, chlorite schist and country rocks (i.e., marble, mica schist, paragneiss, and syenite vein hosted in the paragneiss) were examined. These samples were derived from the new ore prospect at the culmination of Żmijowiec Rib, except mica schist, which was sampled a few hundred meters away, and marble from an abandoned quarry in the Kleśnica valley.

Both newly collected samples and additional samples from the repository at the Institute of Geological Sciences of the University of Wrocław (Wrocław, Poland) were examined. Thin sections were examined in transmitted light under the petrographic microscopes Eclipse E600 POL (Nikon Corporation, Minato-ku, Tokyo, Japan) and Eclipse LV100 POL (Nikon Corporation, Minato-ku, Tokyo, Japan). Selected thin sections were further examined under the electron microprobe (EPMA) Cameca SX FIVE FE, at the Faculty of Geology, the University of Warsaw (Warszawa, Poland). Wavelength dispersive spectrometer (WDS) analyses were performed under the 15 kV accelerating voltage and a variable beam current, and both natural and synthetic standards were used. Minerals with a lower stability under the electron beam (serpentine, carbonate, talc, chlorite, sulfides and arsenides, saponite, apatite, muscovite and biotite, and feldspar; Tables S2–S10, respectively) were measured using a 15 nA current, whereas the more stable phases (spinel, amphibole, clinopyroxene, garnet, titanite, ilmenite and rutile, zircon, and the epidote-group minerals; Tables S11–S18, respectively) were measured using a 20 nA current. In order to differentiate chlorite-group minerals, the classification of Foster [46] with the modifications of Esteban et al. [47], was implemented. Amphiboles are classified according to the scheme of Hawthorne et al. [48], although tremolite is additionally subdivided into actinolite and tremolite [49].

The bulk rock geochemical analyses, hydrogen isotope compositions, and oxygen and carbon isotope compositions of carbonates were determined on powdered samples. Samples were coarsely crushed by a hammer and then powdered in a planetary ball-mill Retsch PM 100, using the 250 mL corundum jar (with the exception of sample KL-6, which was milled in the 125 mL agate jar) at the Faculty of Geology (University of Warsaw, Warszawa, Poland). Several pure mineral splits were obtained from the coarsely crushed material. Bulk rock analyses were conducted at Bureau Veritas Minerals (Vancouver, BC, Canada): major element concentrations were determined by inductively coupled plasma-emission spectrometry (ICP-ES) following the lithium borate method and trace element concentrations were measured via inductively coupled plasma-mass spectrometry (ICP-MS) following digestion in aqua regia or lithium borate method, depending on analysed elements (detection limits are presented in the footnote of the table with chemical analyzes). Chlorine content was measured using instrumental neutron activation analysis (INAA) on bulk rock powders at Maxxam Analytics Laboratories (Vancouver, BC, Canada) of the Bureau Veritas Group Company.

The oxygen, hydrogen, and carbon stable isotope ratios were measured at the University of Texas (Austin, TX, USA) using a ThermoElectron MAT 253 isotope ratio mass spectrometer (IRMS). Bulk rock hydrogen isotope ratios were measured using a Thermo Combustion Elemental Analyzer (TC/EA)

(Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled to the IRMS following the methods of Sharp et al. [50] and calibrated using a set of international reference standards (IAEA-CH7 [51], NBS-22 [51], USGS57 [52], USGS58 [52]) and one in-house working glass standard were analyzed along with the samples. The δD values are reported in per mil notation relative to Standard Mean Ocean Water (SMOW); precision is $\pm 3\text{‰}$. Carbonate samples were placed in 12 mL Exetainer vials, flushed with ultra-high purity helium, and then reacted with 100% H_3PO_4 at 50 °C for 2 h in the case of calcite samples, or 8 h for the dolomite-dominated ones. Headspace CO_2 was analyzed using a Gasbench II (Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled to the IRMS following the methods of Spötl and Vennemann [53]. The $\delta^{18}O$ values were reported relative to Standard Mean Ocean Water (SMOW), whereas $\delta^{13}C$ values are reported relative to the Pee Dee Belemnite (PDB). Analytical precision is $\pm 0.2\text{‰}$ and $\pm 0.1\text{‰}$ for $\delta^{18}O$ and $\delta^{13}C$ values, respectively. For the oxygen isotope analyses of silicates (serpentine, chlorite and amphibole), separates were rinsed in dilute HCl to remove carbonates, hand-picked under a binocular microscope in order to ensure a homogeneous sample (i.e., free of inclusions), and analyzed for oxygen isotope compositions using the laser fluorination method of Sharp [54]. Samples were heated with a New Wave Research MIR10-30 laser (MKS Instruments Inc., Andover, MA, USA) in the presence of BrF_5 and purified O_2 was then introduced into the IRMS. The garnet standard UWG-2 ($\delta^{18}O$ value = $+5.8\text{‰}$ [55]), and in-house quartz standard Lausanne-1 ($\delta^{18}O$ value = $+18.1\text{‰}$) were also analyzed in order to check the precision and accuracy of analyses. The measured $\delta^{18}O$ values are reported relative to SMOW; analytical precision is $\pm 0.1\text{‰}$ (1σ).

4. Field Observations

Detailed field observations, including schistosity orientation, were performed in the newly discovered ore body at the Żmijowiec Rib (Figure 3A), as well as in the well-known Kletno deposit. Country metasediments, as well as serpentinite, all have a well-developed schistosity (Figure 3B,C). A few tens of meters from the serpentinite, paragneiss hosts syenite, syenogranite and pegmatite veins (Figure 3C). The diameter of these veins reaches a few tens of centimeters, although few hundred meters away from the studied ore body, the exposed width of these veins can reach a few meters.

The serpentinite contains NW-trending chlorite schist zones, typically a few tens of centimeters thick. Near the eastern margin of the serpentinite outcrop, the thickness of the chlorite schist bodies reaches a few meters. In addition, the chlorite schist contains lenses of hornblende and epidote hornblende. Along the eastern and northeastern margin of the serpentinite body (near the zone rich in chlorite schist and hornblende bodies), loose blocks of epidote hornblende, dolomite vein and talc schist are common, however, contacts of these rocks with the serpentinite are concealed beneath quaternary sedimentary cover. Talc schist blocks lack macroscopically-visible contacts with other lithologies. In some thick dolomite vein fragments, sharp or slightly gradational contact with the chlorite schist can be observed, thus thick dolomite veins are interpreted as hosted in the chlorite schist and not in serpentinite (in contrast to microscopic dolomite veins). Near the western edge of the serpentinite body, large blocks of metagabbro and metadiabase are common (Figure 2), but also lack visible contacts with other lithologies. The closest observed in situ country rock occurrences are two outcrops of paragneiss located to the south and southwest of serpentinite. Within these paragneiss bodies, syenite, syenogranite and pegmatite veins, separated from the host-gneiss by a thin mica layer, are common.

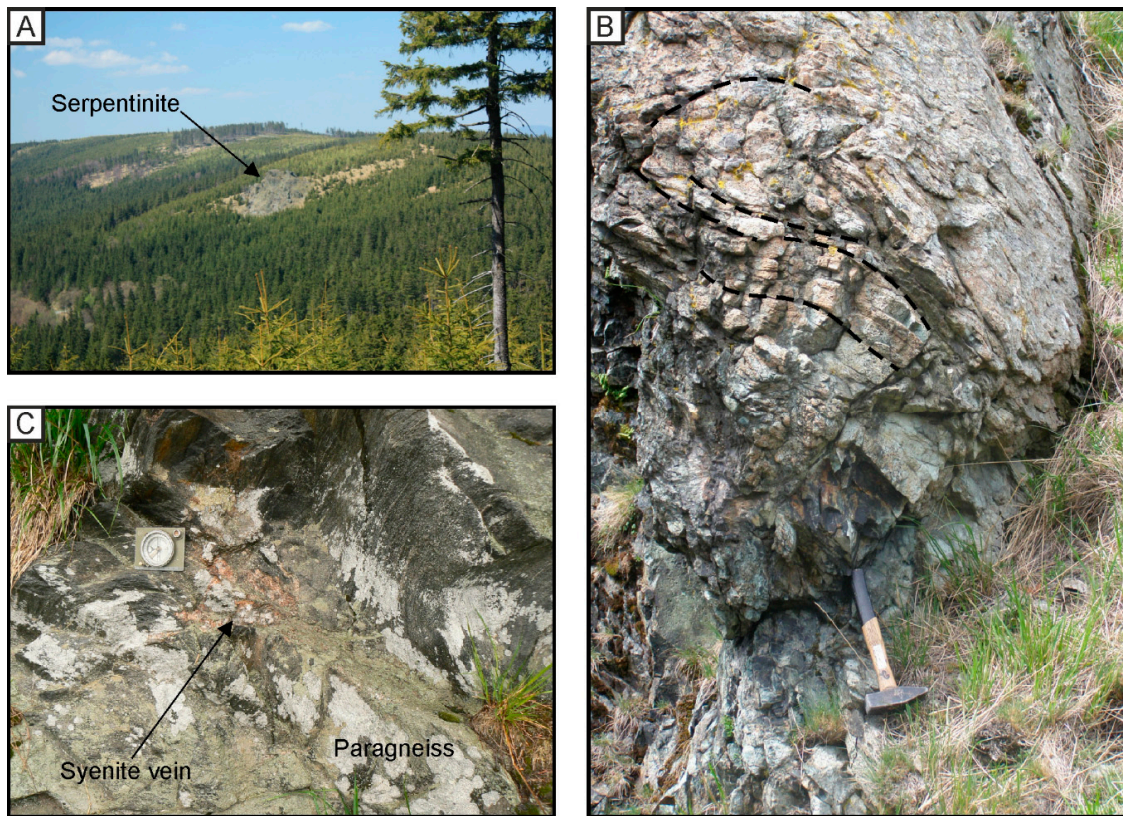


Figure 3. Examples of field occurrences. (A) Serpentine outcrop at the Żmijowiec Rib (photo taken from the top of Mount Śnieżnik); (B) Schistosity in serpentinite (selected planes are highlighted); (C) Syenite vein in the country paragneiss few tens of meters away from serpentinite.

The schistosity orientation in serpentinite has two major and one minor directions (Figure 4A; Table S1): $71/58$ ($n = 30$), $118/60$ ($n = 22$), and $166/74$ ($n = 3$). Measurements of the schistosity in the neighboring paragneiss ($n = 21$) show a dominant dip direction of $72/55$ (Figure 4B), thus being nearly identical to the commonly observed schistosity orientation in the serpentinite. Measurements in the chlorite schist show a high scatter (Figure 4C), which may be caused by the limited data ($n = 7$). However, the scatter can be caused also by deformation of the host rock, before its emplacement into the continental crust.

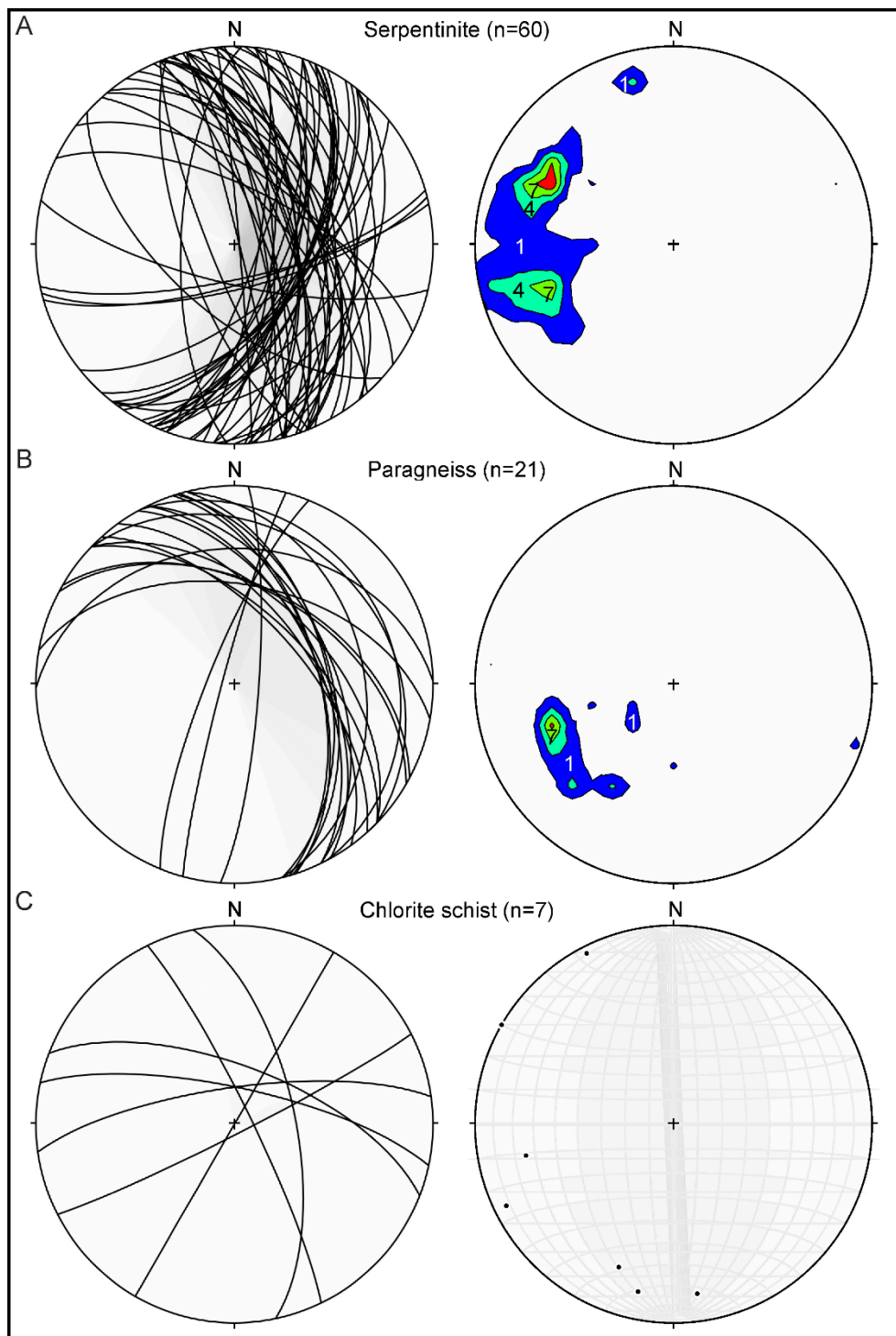


Figure 4. Schistosity orientation presented on a lower hemisphere projection (stereograms developed in Stereonet v. 10.2.8 software). Left panels—structures presented as planes, right panels—presented as poles to planes (C) or density plots for poles to planes (A, B; contours per 1% area: 1, 4 and 7%). (A) Serpentinite; (B) Adjacent paragneisses; (C) Serpentinite-hosted chlorite schists.

5. Petrography and Mineral Chemistry

Examined samples are described in brief in Table 1. Macroscopic photographs are presented in Figure 5, and microphotographs and BSE images of the selected structures and minerals in Figure 6. The chemical compositions of minerals are presented in Tables S2–S18.

Table 1. Description of the examined samples from the Kletno deposit.

Lithology	Sample	Description	Composition	Accessory Minerals
<i>The culmination of the Żmijowiec Rib (a newly recognized ore prospect)</i>				
Serpentinite	KL-4, KL-4A, KL-4B, KL-4C	Green, blue or black antigorite serpentinite with non-pseudomorphic texture; fine serpentine needles (chrysotile or fibrous antigorite) sparse in the matrix; chromite occurs as rounded, broken grains with carbonate and tremolite infill of cracks; chrysotile veins are being cut by tremolite veins, whereas both type of veins are being cut by calcite (few tens of μm thick) and dolomite ($<3\ \mu\text{m}$ thick) veins; in places, tremolite and carbonate veins contain talc; some pyrrhotite grains contain pentlandite exsolution lamellae	Antigorite, chrysotile, calcite, tremolite, chromite	Dolomite, magnetite, ilmenite, pyrrhotite, pentlandite, iron sulfide (pyrite or marcasite), nickeline
Talc schist	KL-13	Dark green or yellowish to brown-colored, fine-grained talc rock with the well-developed foliation or schistosity; penninite nests are being replaced by amphibole needles or short prisms, or talc blades; Fe, Ni-oxides and hydroxides, with variable Cr, Al and Si admixture, likely form pseudomorphs after Cr-spinel, these pseudomorphs probably formed under hypergenic or low-temperature hydrothermal conditions	Talc, penninite, tremolite (both tremolite and actinolite), anthophyllite	Ilmenite, Fe, Ni-oxides/hydroxides
Chlorite schist	KL-5, KL-5A	Greenish-gray well-foliated rock; a few tens of μm in size ilmenite grains, with subhedral or skeletal habit, are often arranged in aggregates; up to ca. 10 mm in size, euhedral magnetite likely postdates ilmenite, within this magnetite, chlorite, ilmenite and bornite inclusions are present; the youngest phase observed is chrysotile	Chlorite (clinochlore and subordinate penninite), ilmenite, magnetite	Chrysotile, zircon, bornite

Table 1. Cont.

Lithology	Sample	Description	Composition	Accessory Minerals
Hornblendite and epidote hornblendite	KL-1, KL-1D, KL-11	Gray to green or black, with a yellowish-creamy carbonate intercalations up to ~5 mm in size; amphibole crystals up to 10 mm long, these amphiboles composition vary significantly between samples and in sample-scale, some amphibole crystals are zoned, i.e., tremolite core enveloped by pargasite, and then, in places, by an outermost magnesio-hastingsite or pargasite rim; some epidote-clinozoisite crystals show zoning or contain allanite inclusions; fragmented or corroded almandine-grossular garnet crystals are often enclosed in amphiboles, ilmenite or calcite, whereas andradite-grossular garnet occurs as the fine, relic inclusions within epidote-clinozoisite crystals; some magnetite crystals contain ilmenite exsolution lamellae, whereas other are being mantled by a thin, Mn-rich ilmenite rims; chalcopyrite contains minute galena inclusions, while apatite is rich in chlorite inclusions	Amphiboles (pargasite and ferro-pargasite, subordinate ferro-sadanagaite, magnesio-hastingsite and tremolite-resembling actinolite), epidote-clinozoisite solid-solution, chlorite (ripidolite and brunsvigite), diopside, titanite, saponite, almandine-grossular garnet, ilmenite, magnetite, calcite	Andradite-grossular garnet, opal, zircon, apatite, chalcopyrite, galena
Dolomite vein	KL-3, KL-3A, KL-3B, KL-3C	Creamy, yellowish or brownish, cryptocrystalline to coarse-grained dolomite veins; clinocllore occurs as individual blades, aggregates and the fine-grained nests—monomineral and chlorite-carbonate nests, in places gradual transitions from chlorite nests to fine-grained carbonate nests; chlorite nests, resembling habit of dolomite crystal, are interpreted as pseudomorphs; small, euhedral carbonate crystals present in the chlorite nests, whereas fine-grained chlorite-carbonate nests contain minute magnetite or apatite; apatite crystals often contains calcite inclusions, ilmenite encloses magnetite and zircon, while magnetite contains clinocllore, carbonate and talc inclusions, as well as ilmenite exsolution lamellae	Dolomite, calcite, chlorite (clinocllore), talc, ilmenite, magnetite	Apatite, hematite, zircon, thorite

Table 1. Cont.

Lithology	Sample	Description	Composition	Accessory Minerals
Metagabbro (KL-2) and metadiabase (KL-6)	KL-2, KL-6	Bright to dark gray, fine- to medium-grained, in places ophitic or subophitic; chlorite occurs as fine-grained nests or coarser blades, the latter often enclosed within clinozoisite crystals, chlorites are apparently replaced by amphibole and clinozoisite, in places, chlorite nests are replaced by fine-fibrous amphiboles (resembling nephrite under the microscope, i.e., nephritic texture); rutile occurs in the chlorite aggregates, whereas fine labradorite relics in the muscovite aggregates	Clinozoisite, chlorite (clinocllore and subordinate sheridanite), amphiboles (pargasite, magnesio-hornblende and tremolite-resembling actinolite), muscovite, titanite	Plagioclase (labradorite), rutile, carbonate, barite
Paragneiss	KL-10	Grayish, well-foliated and locally banded gneiss (some bands contain both felsic and mafic minerals, whereas other bands mafic minerals only); in places, rotated and fractured, feldspar or quartz porphyroblasts occur; magnetite and hematite contain ilmenite exsolution lamellae; allanite contains ilmenite, apatite and monazite inclusions, whereas feldspar porphyroblasts contain ilmenite, quartz and minute feldspar inclusions	Quartz, K-feldspar, plagioclase (albite and oligoclase), muscovite, biotite, F-apatite, magnetite, hematite	Ilmenite, allanite, monazite
Mica schist	KL-14	Reddish-gray, medium-grained rock with a well-developed schistosity; coarse garnet is often enveloped by biotite or muscovite, garnet also contains biotite, quartz, ilmenite and apatite inclusions	Quartz, feldspar, muscovite, biotite, garnet	Apatite, ilmenite, magnetite
Syenite	KL-9	Creamy to pink, coarse-grained, in places pegmatitic syenite; K-feldspar crystals show polysynthetic twinnings of microcline type, albite contains K-feldspar exsolution lamellae, some feldspars are altered to kaolinite or saussurite; quartz contains feldspar or minute quartz inclusions; muscovite is arranged in stacks or acicular, fan-shaped prisms; ilmenite contains exsolution lamellae and rims of rutile; ilmenite-apatite aggregates are present, in which apatite is mantled by discontinuous rims of zircon grains	Quartz, K-feldspar, plagioclase (albite), muscovite, chlorite (brunsvigite and subordinate ripidolite), apatite, ilmenite, magnetite	Titanite, zircon, rutile

Table 1. Cont.

Lithology	Sample	Description	Composition	Accessory Minerals
<i>The Klešnica stream valley in the Kletno village (the well-known Kletno deposit)</i>				
Calcite marble	KL-12, KL-12A, KL-12F	White, gray or creamy, medium-grained marble; foliation is defined by the presence of parallel fine-grained and medium-grained layers, as well as quartz-free and quartz-bearing layers, in these layers quartz occurs as rounded grains—smaller than calcite; a later quartz-calcite veins cut the rock; pyrite usually occurs as regular (subhedral) or framboidal (partially-replaced by calcite) crystals, and as hexagonal pseudomorphs (probably after pyrrhotite or troilite)	Calcite, quartz, saponite, chlorite	Cl-apatite, pyrite

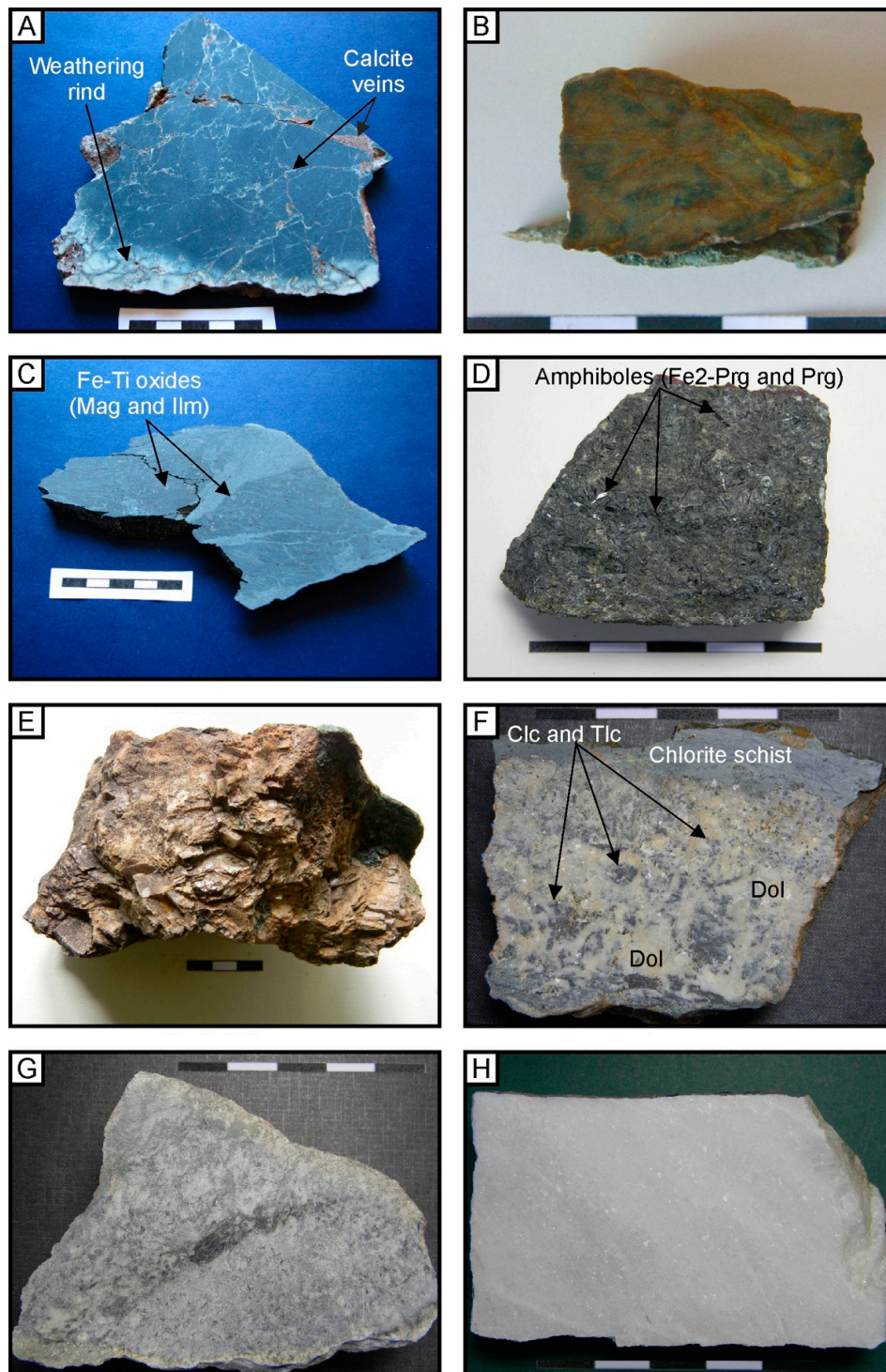


Figure 5. Hand-specimen photographs. (A) Serpentinite sample KL-4 with visible creamy weathering rind; (B) Brownish colored talc schist; (C) Chlorite schist (KL-5) with macroscopically visible magnetite and ilmenite crystals; (D) Coarse-grained hornblende sample, most abundant in Fe, Ti, V and Cu (KL-1); (E) Barren dolomite vein (KL-3) with visible coarse dolomite crystals and contact with chlorite schist; (F) Mineralization-bearing dolomite vein (KL-3C); (G) Medium- to coarse-grained barren metagabbro (KL-2); (H) Calcic Biała Marianna marble (KL-12) from quarry near the Jaskinia Niedźwiedzia (the Bear Cave). Abbreviations: Clc—clinochlore, Dol—dolomite, Fe2-Prg—ferro-pargasite, Ilm—ilmenite, Mag—magnetite, Prg—pargasite, Tlc—talc. The scale bar length is: 5 cm—(A,C); 10 cm—(B,D,F–H); 3 cm—(E).

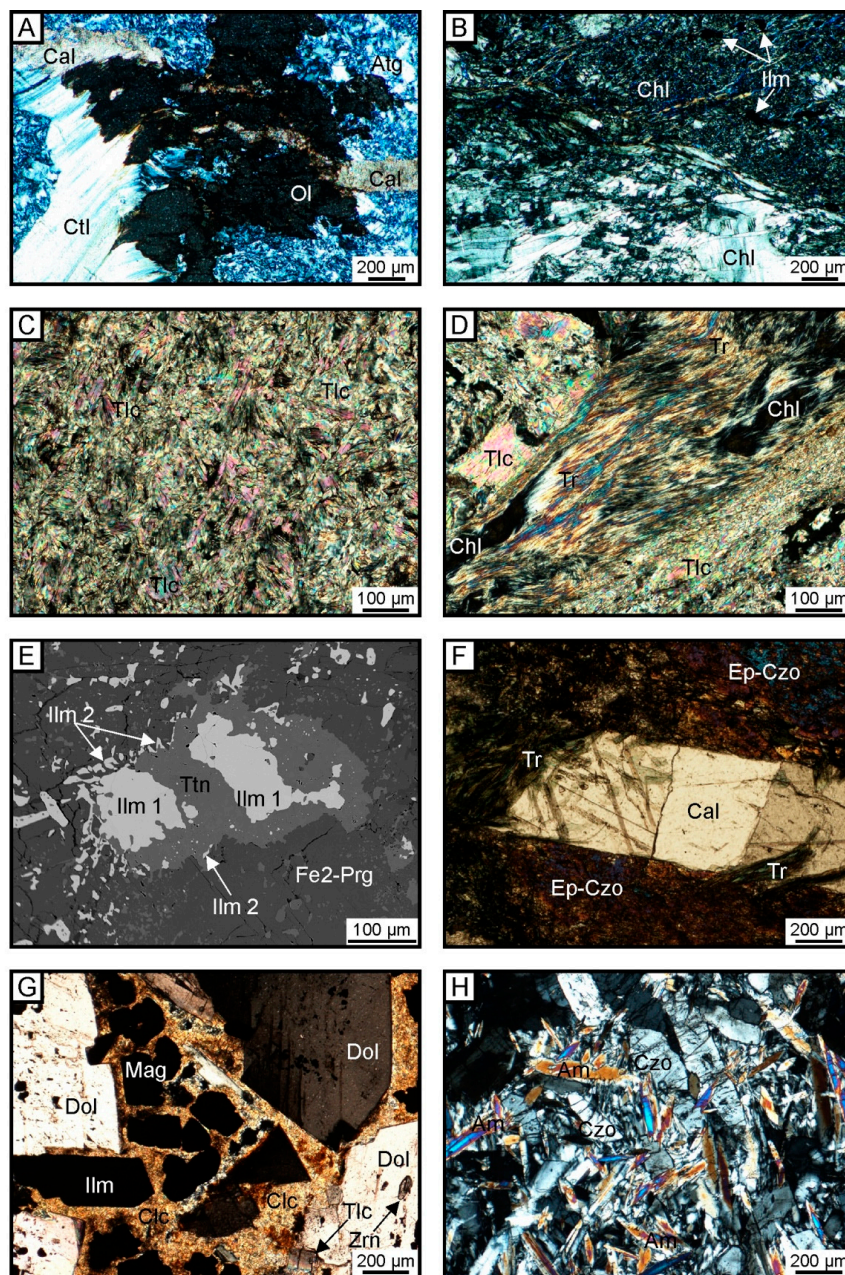


Figure 6. Microphotographs (A–D,F–H) and BSE image (E) of the studied samples. (A) An antigorite serpentinite cut by chrysotile and calcite veins, at which margins crystallized an olivine related with deserpentinization; (B) Fine- and coarse-grained zones in the chlorite schist KL-5; (C) A medium-grained groundmass of the talc schist KL-13; (D) A fibrous tremolite vein (probably a shear zone relic) cutting the talc schist (KL-13); (E) BSE image of a relic igneous ilmenite (Ilm 1 = ilmenite 1), partially-replaced by a metamorphic titanite, and then probably also by the secondary metamorphic ilmenite (Ilm 2 = ilmenite 2), hosted in hornblende KL-1; (F) A calcite vein cutting the epidote-clinozoisite groundmass, which are then partially-replaced by tremolite needles (epidote hornblende KL-11); (G) The fine-grained clinochlore filling spaces between the coarse dolomite, as well as fine- to medium-grained magnetite, ilmenite and talc crystals (mineralized dolomite vein KL-3C); note the fine zircon inclusion within the coarse dolomite; (H) A barren metagabbro (KL-6) groundmass composed of amphiboles and clinozoisite. Abbreviations: Am—amphibole-super group minerals; Atg—antigorite, Cal—calcite, Chl—chlorite-group minerals, Clc—clinochlore, Ctl—chrysotile, Czo—clinozoisite, Dol—dolomite, Ep-Czo—epidote-clinozoisite solid-solution, Fe2-Prg—ferro-pargasite, Ilm—ilmenite, Mag—magnetite, Ol—olivine, Tlc—talc, Tr—tremolite, Ttn—titanite, Zrn—zircon.

5.1. Serpentinite

The cryptoblastic serpentinite (Figure 3B) is cut by macroscopic calcite veins (sample KL-4; Figure 5A) and hosts white tremolite veins or nests (KL-4C). Based on non-pseudomorphic fabric, typical of higher metamorphism grade serpentinites, the antigoritic composition of serpentinite is consistent with the earlier description of this outcrop [10]. Chromite represents nearly pure Fe^{2+} -Cr-spinel (Table S11). In addition, pentlandite (Table S6) grains occur along thin ($<3\ \mu\text{m}$) dolomite veins, whereas secondary olivine occurs at the margins of thicker chrysotile or calcite veins (Figure 6A). According to Smulikowski et al. [10], the secondary olivine is more ferrous than the antigorite groundmass, and its composition is consistent with deserpentinization at temperatures of ca. 400–500 °C.

5.2. Talc Schist

The talc schist (Figure 5B) also contains penninite (Figure 7; Tables S4 and S5). Larger concentrations of talc form the interlocking non-pseudomorphic fabric sensu Wicks and Whittaker [56] (Figure 6C), whereas penninite aggregates form interlocking and interpenetrating fabric. In addition, talc, penninite, and tremolite veins are present. In the latter, the tremolite crystals orientation is parallel or nearly parallel to the vein propagation (Figure 6D). Anthophyllite occurs as individual, euhedral crystals, or as tremolite-anthophyllite grains, in which the core is tremolite and the discontinuous rim is anthophyllite. These zoned amphibole grains are rimmed by talc, which then makes contact with the tremolite fibers of the vein matrix.

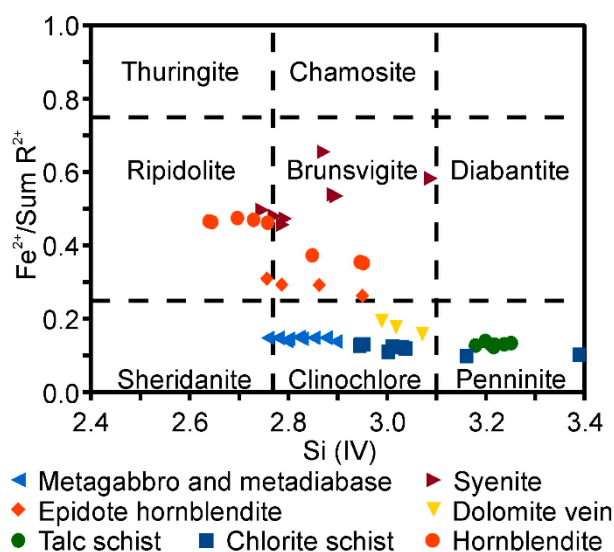


Figure 7. Chlorite-group minerals composition at the chlorites classification diagram of Foster [46], with modifications by Esteban et al. [47].

5.3. Chlorite schist

The chlorite schist (Figure 5C) is predominantly composed of clinochlore and subordinate penninite (Figure 7; Table S5), which are arranged in the interlocking non-pseudomorphic fabric, although secondary chlorite veins and nests show interpenetrating fabric (Figure 6A). The abundant presence of the Fe-Ti-V mineralization is manifested by fine ilmenite grains (average content of $\text{V}_2\text{O}_3 = 0.3\ \text{wt. \%}$; Table S16), and coarse, euhedral magnetite crystals (up to $\sim 10\ \text{mm}$; $0.27\ \text{wt. \%}$ V_2O_3 in average; Table S11).

5.4. Hornblendite and Epidote Hornblendite

The hornblendite (KL-1, KL-1D; Figure 5D) and epidote hornblendite (KL-11) samples vary in terms of the grain size, ranging from fine to coarse. The hornblendites lack foliation or schistosity and have the same mineralogy, although the mineral modal abundances, as well as chemical composition of individual crystals, vary. The abundance of epidote-group minerals is the basis for subdivision into hornblendite and epidote hornblendite. Also, chlorite-group minerals (Figure 7) abundance vary significantly. Two generations of ilmenite (0.48 wt. % V_2O_3 on average) are present: 1) primary magmatic ilmenite, which is preserved as small, relic grains embedded within coarse titanite crystals and 2) metamorphic ilmenite, which discontinuously rim the titanite (titanite contains 0.38 wt. % V_2O_3 on average; Figure 6E; Tables S15 and S16). Magnetite has the highest concentration of V (V_2O_3 = 0.85 wt. % on average; Table S11), whereas the V content in almandine-grossular garnet (0.38 wt. % V_2O_3 ; Table S14) is similar as in titanite. Calcite replaces chlorite and epidote-clinozoisite, although this calcite is replaced by amphiboles in places (Figure 6F), and the amphiboles are cut by younger calcite veins (Table S3). Within the calcite veins, magnetite and ilmenite grains are present (Tables S2 and S16).

5.5. Thick Dolomite Veins

A few centimeter thick dolomite veins occur within the chlorite schist. These are different from the very thin (<3 μm) dolomite veinlets present in the serpentinite and <1 mm thick calcite veins also present in serpentinite. The thick dolomite veins occur as both nearly monomineral (sample KL-3; Figure 5E) and heterogeneous veins (KL-3C). The heterogeneous veins are composed of macroscopic carbonate, magnetite and ilmenite (average 0.87 and 0.37 wt. % V_2O_3 , respectively; up to ~3 mm in diameter; Tables S11 and S16), clinocllore, and talc (Figure 5F). Dolomite in veins occurs as nearly cryptocrystalline, compact masses, or euhedral crystals with diameters of 30–40 mm (Figure 5E). In addition to dolomite, minor calcite is present in the form of fine-grained aggregates, filling spaces between dolomite crystals (Figure 6G; Table S3). Talc and clinocllore (Figure 7; Tables S4 and S5), as well as magnetite, occur in variable proportions. Zircon (Figure 6G; Table S17), present in the dolomitic matrix, has a mosaic inner structure and it can contain U-rich thorite exsolutions or is associated with elongated tails that are composed of fine magnetite grains. In addition, a comparable dolomite vein from the Naławice quarry, within the serpentinites of the Central-Sudetic Ophiolite, was sampled from the antigorite serpentinites of the Ślęza Ophiolite. The dolomite vein is spatially-associated with a few tens of cm thick chrysotile veins, and similar to the dolomite veins from Kletno is magnetite-bearing.

5.6. Metagabbro and Metadiabase

Two barren (lacking extensive ilmenite and magnetite mineralization) metabasites were studied: fine-grained equigranular metadiabase (KL-6) and coarse-grained heterogranular metagabbro, with preserved ophitic or subophitic texture in places (KL-2; Figure 5G). Regardless of textural features, most samples have similar mineralogy (Table 1), i.e., the most abundant constituents are clinozoisite, amphiboles, titanite and aggregates of the fine-grained muscovite (Table S9) and chlorite (Figure 7; Table S5). Clinozoisite is often rimmed by needle-shaped amphibole, which resembles uralite (Figure 6H).

5.7. Marble

The calcitic marble called Biała Marianna (Figure 5H) is a medium-grained, foliated rock. In addition to calcite, quartz, saponite, chlorite, apatite and pyrite are present. Jastrzębski [20] also noted the presence of dolomite, phlogopite, biotite and tremolite in marbles from this area, as well as distinguished the calcite–dolomite marble variety.

5.8. Paragneiss and Mica Schist

The paragneiss (KL-10; Figure 3C) has a well-developed schistosity or foliation, and is locally banded. It is composed of quartz, K-feldspar, plagioclase, muscovite, biotite, apatite, magnetite, hematite and accessory minerals (ilmenite, allanite, and monazite; Table 1). The mica schist is characterized by schistosity defined by parallel biotite and muscovite flakes, which suggests the syn-tectonic character of biotite and muscovite. Garnet is absent in the examined paragneiss, whereas in the mica schist, garnets form the largest crystals observed and are distributed unevenly without correlation with the rock fabric. This suggests post-tectonic or late-tectonic growth of garnet. Quartz, feldspar, muscovite, and biotite are also abundant.

5.9. Syenite Veins

The syenite occurs within the paragneiss adjacent to serpentinite (Figure 3C). The syenite is coarse grained, in places pegmatitic, and its composition varies from syenite to syenogranite. K-feldspar grains are up to 30–40 mm in length, whereas quartz is up to a few mm in length. Chlorite (Figure 7; Table S5) occurs as medium blades, often arranged in stacks or layers, in which titanite is common. The observed spatial-relations of titanite, ilmenite, rutile, apatite and zircon do not allow for precise determination of these minerals crystallization sequence in the syenite.

6. Bulk Rock Chemical and Stable Isotope Compositions

6.1. Bulk Rock Chemical Compositions

The bulk chemical compositions of samples from Kletno are presented in Table 2. The iron content of serpentinite (6.53–7.14 wt. % Fe_2O_3 = 4.57–4.99 wt. % Fe) and talc schist (6.27 wt. % Fe_2O_3 = 4.39 wt. % Fe) are typical of altered peridotites. The highest Fe contents were noted for lithologies containing abundant Fe-Ti-V mineralization, i.e., chlorite schist (15.98 wt. % Fe_2O_3 = 11.18 wt. % Fe), hornblendites (14.19–20.12 wt. % Fe_2O_3 = 9.92–14.07 wt. % Fe) and the mineralized dolomite vein (10.18 wt. % Fe_2O_3 = 7.12 wt. % Fe). Iron contents are much lower in the barren dolomite vein (non-mineralized dolomite vein; 4.04 wt. % Fe_2O_3 = 2.83 wt. % Fe) and metagabbro (4.36 wt. % Fe_2O_3 = 3.05 wt. % Fe), and the lowest in marble (0.06–0.07 wt. % Fe_2O_3 = 0.04–0.05 wt. % Fe). Iron contents comparable with some of the mineralized samples are reported for country mica schist and paragneiss (11.76–12.30 wt. % Fe_2O_3 = 8.23–8.60 wt. % Fe), whereas the syenite is characterized by a very low content (1.30 wt. % Fe_2O_3 = 0.91 wt. % Fe). For comparison, the average Fe content of a Fe-Ti-V mineralized metabasites of the Ślęza Ophiolite, i.e., the best recognized magmatic Fe-Ti-V deposit in the Sudetes, is 14.21 wt. % [57], equal to the most Fe-abundant hornblendites from Kletno.

The titanium content in serpentinite (0.01–0.03 wt. % TiO_2 = 0.006–0.018 wt. % Ti) is low, slightly higher in the talc schist (0.09 wt. % TiO_2 = 0.054 wt. % Ti), and significantly higher in the mineralized rocks: chlorite schist (1.42 wt. % TiO_2 = 0.851 wt. % Ti), hornblendites (0.91–3.42 wt. % TiO_2 = 0.545–2.050 wt. % Ti), mineralized dolomite vein (1.38 wt. % TiO_2 = 0.827 wt. % Ti); the latter contrasting with the barren dolomite vein (<0.01 wt. % TiO_2). Metagabbro is poor in Ti (0.06–0.21 wt. % TiO_2 = 0.034–0.126 wt. % Ti), and in marble the Ti content is below the detection limit (<0.01 wt. % TiO_2), similar as in the barren dolomite vein. However, the country mica schist and paragneiss (1.33–2.95 wt. % TiO_2 = 0.797–1.768 wt. % Ti) contain Ti in amount comparable with the mineralized lithologies, whereas syenite (0.45 wt. % TiO_2 = 0.270 wt. % Ti) is relatively poor in Ti. According to Wiszniewska and Petecki [57], an average Ti content of the Fe-Ti-V-mineralized metabasites from the Ślęza Ophiolite (4.92 wt. % TiO_2 = 2.949 wt. % Ti) is higher than those of the mineralization-bearing rocks from Kletno, although comparable to the most Fe-enriched mineralization-bearing rocks from Kletno. However, Ti contents of both the newly recognized ore prospect in Kletno and mineralized metabasites of the Ślęza Ophiolite, according to the recent state of knowledge, do not meet the minimum content criteria for the magmatic Fe-Ti deposits, and thus remain uneconomic.

Table 2. The bulk-rock chemical composition of studied rocks from Kletno in the Śnieżnik Massif.

Oxide/ Element	Serpentine		Talc Schist	Chlorite Schist	Hornblendites			Dolomite Vein		Metabasite		Marble		Gneiss	Mica Schist	Syenite
	KL-4	KL-4C	KL-13	KL-5	KL-1	KL-1D	KL-11	KL-3	KL-3C	KL-2	KL-6	KL-12	KL-12F	KL-10	KL-14	KL-9
SiO ₂ (wt. %)	43.88	43.84	50.86	30.59	28.23	32.72	38.59	0.76	0.72	42.06		15.28	15.21	48.61	41.87	62.84
Al ₂ O ₃	2.27	2.28	6.23	12.22	12.28	14.26	11.37	0.01	0.15	21.83		0.08	0.15	19.32	29.97	18.97
Fe ₂ O _{3total}	6.53	7.14	6.27	15.98	20.12	15.15	14.19	4.04	10.18	4.36		0.07	0.06	12.3	11.76	1.3
MgO	33.90	33.1	26.55	28.14	9.09	11.78	11.73	18.79	17.18	10.80		1.53	1.47	2.35	2.01	0.23
CaO	0.28	0.24	1.84	0.02	15.30	15.42	15.14	30.22	28	15.74		46.52	46.12	1.55	0.50	0.33
Na ₂ O	<0.01	<0.01	0.02	<0.01	0.90	1.03	0.9	<0.01	<0.01	0.63		<0.01	<0.01	1.22	1.23	1.71
K ₂ O	<0.01	<0.01	<0.01	<0.01	0.35	0.21	0.17	<0.01	<0.01	0.39		<0.01	<0.01	7.72	6.54	13.21
TiO ₂	0.03	0.01	0.09	1.42	3.42	1.03	0.91	<0.01	1.38	0.21	0.057	<0.01	<0.01	2.95	1.33	0.45
P ₂ O ₅	<0.01	<0.01	<0.01	<0.01	0.23	0.15	0.13	<0.01	0.16	<0.01	<0.002	0.01	<0.01	0.87	0.22	0.11
MnO	0.04	0.07	0.07	0.10	0.24	0.20	0.2	0.55	0.46	0.10		0.02	0.02	0.06	0.58	0.008
LOI	12.00	12.2	7.0	10.90	9.20	7.60	6.3	45.2	41.3	3.50		36.4	36.90	2.8	3.6	0.6
Total	98.93	98.88	98.93	99.37	99.36	99.55	99.63	99.57	99.53	99.62		99.91	99.93	99.75	99.61	99.758
TOT/C	0.18	0.11	0.03	0.03	1.93	1.29	0.81	13.07	12.05	0.03		10.87	10.76	0.02	0.45	0.03
TOT/S	0.07	0.08	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cr (ppm)	2004.7	2470	2449.5	88.9	<13.7	<13.7	<13.7	<13.7	54.7	109.5	115.9	<13.7	<13.7	<13.7	150.5	4.5
Ba	1	<1	4	2	7	9	9	<1	<1	21	3	3	5	422	941	847
Ni	1747	1876	1835	183	62	63	66	50	101	172	146.8	1.1	<0.1	26	64	3.3
Sc	9	6	9	28	48	60	82	8	21	25	14.8	<1	<1	10	25	1
Be	<1	<1	<1	<1	<1	<1	<1	<1	<1	2	0.2	<1	<1	3	6	3
Co	87.3	94.8	79.9	94.0	77.5	53.9	57.6	16.7	29.5	27.8	22.1	<0.2	<0.2	19.4	36.9	2.3
Cs	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.06	<0.1	<0.1	3.1	7.6	0.7
Ga	1.1	1.4	7.4	6.7	12.2	13.8	12.1	<0.5	<0.5	13.2	5.3	<0.5	<0.5	27.4	38.5	7.5
Hf	<0.1	<0.1	0.2	0.7	0.7	1.7	1.7	<0.1	2	1.0	<0.02	<0.1	<0.1	13.6	5.7	1.2
Nb	<0.1	<0.1	0.6	3.2	3.1	3.0	2.5	<0.1	3.1	1.0	<0.02	<0.1	<0.1	133.1	22.9	16.8
Rb	<0.1	0.3	0.7	<0.1	1.0	0.6	0.9	<0.1	<0.1	13.0	2.5	<0.1	<0.1	97.7	219.6	87.4
Sn	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0.1	<1	<1	4	6	0.2
Sr	6.9	3.2	4.6	<0.5	268.9	182.5	119.4	730	440	1021.8	189.6	163.0	154.8	121.1	106.7	815
Ta	<0.1	<0.1	<0.1	0.2	0.3	0.2	0.2	<0.1	<0.1	0.1	<0.05	<0.1	<0.1	8.1	1.8	1.4
Th	<0.2	<0.2	<0.2	<0.2	<0.2	0.6	0.5	<0.2	<0.2	0.3	<0.1	<0.2	<0.2	12.2	28.0	1.1
U	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	1	3.9	0.1
V	54	54	73	463	2055	836	765	<8	270	142	62	<8	<8	120	166	16

Table 2. Cont.

Oxide/ Element	Serpentinite		Talc Schist	Chlorite Schist	Hornblendites			Dolomite Vein		Metabasite		Marble		Gneiss	Mica Schist	Syenite
	KL-4	KL-4C	KL-13	KL-5	KL-1	KL-1D	KL-11	KL-3	KL-3C	KL-2	KL-6	KL-12	KL-12F	KL-10	KL-14	KL-9
W	0.6	<0.5	<0.5	0.7	0.9	<0.5	0.9	<0.5	<0.5	<0.5	<0.1	<0.5	<0.5	0.6	2.4	<0.1
Zr	1.0	2.2	9.9	22.7	22.0	55.9	51.9	0.2	70.9	34.3	0.4	0.7	0.9	586.9	206.7	56.6
Y	0.8	1.1	1.1	0.9	8.9	20.3	29	15.3	13	10.0	3.38	1.3	1.5	39.8	55.1	6
La	0.3	0.4	0.7	0.3	3.5	6.7	6.2	6.2	3.3	3.7	0.9	0.7	0.9	84.8	83.7	6.2
Ce	0.4	0.8	0.9	0.7	7.2	14.4	14.7	12.7	8.1	7.3	1.5	0.8	1.4	184.5	151.8	16.4
Pr	0.04	0.05	0.11	0.06	0.94	1.83	2.1	1.44	1.01	0.90		0.11	0.17	19.44	17.87	1.74
Nd	<0.3	<0.3	0.5	<0.3	4.7	8.2	10	6.1	4.7	4.1		0.5	0.6	72	65.5	7.2
Sm	0.05	<0.05	0.13	<0.05	1.11	2.22	2.87	1.31	1.39	1.02		0.08	0.10	12.41	12.09	1.4
Eu	<0.02	<0.02	0.02	<0.02	0.74	1.01	0.67	0.67	0.62	0.59		0.03	0.04	3.87	2.96	0.69
Gd	0.08	0.11	0.20	0.13	1.56	3.08	3.93	1.85	1.99	1.35		0.18	0.18	10.68	10.88	1.43
Tb	0.01	0.02	0.03	0.02	0.26	0.57	0.78	0.32	0.37	0.25		0.02	0.03	1.55	1.64	0.21
Dy	0.11	0.16	0.21	0.16	1.65	3.75	5.15	2.18	2.29	1.82		0.18	0.19	8.12	9.23	1.23
Ho	<0.02	0.04	0.05	0.03	0.34	0.82	1.17	0.58	0.53	0.38		0.04	0.03	1.53	1.92	0.22
Er	0.07	0.12	0.11	0.11	1.06	2.43	3.47	1.67	1.57	1.07		0.11	0.13	4.49	5.84	0.64
Tm	<0.01	0.02	0.02	<0.01	0.15	0.33	0.49	0.26	0.21	0.15		0.01	<0.01	0.61	0.80	0.09
Yb	0.08	0.13	0.13	0.10	0.93	2.16	2.94	2	1.5	0.98		0.09	0.08	3.91	4.89	0.51
Lu	0.01	0.02	0.02	0.01	0.15	0.35	0.45	0.31	0.27	0.15		0.01	<0.01	0.55	0.73	0.07
Mo	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.01	<0.1	<0.1	<0.1	0.4	<0.01
Cu	10.7	28.3	1.9	2.8	173.7	0.4	0.7	0.3	0.5	67.4	91.79	0.5	0.4	2	12.4	2.32
Pb	0.3	0.5	0.3	<0.1	4.8	2.6	1.6	5	4.7	2.6	3.88	7.1	7.3	1	6.7	1.6
Zn	25	25	18	32	53	35	36	7	10	10	19.1	8	6	89	54	10.5
As	84.6	3.3	5.7	0.7	0.6	0.6	<0.5	1.8	1.3	<0.5	0.2	<0.5	<0.5	<0.5	1.3	0.2
Cd	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	0.1	0.2	<0.1	0.05	<0.1	<0.1	<0.1	<0.1	<0.01
Sb	0.6	0.4	<0.1	<0.1	<0.1	0.1	0.3	0.1	0.2	<0.1	0.06	0.2	0.2	<0.1	<0.1	0.04
Bi	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.02	<0.1	<0.1	<0.1	0.6	0.04
Ag	<0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	0.12	<0.1	<0.1	<0.1	<0.1	<0.002
Hg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.005	<0.01	<0.01	<0.01	<0.01	<0.005
Tl	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.02	<0.1	<0.1	<0.1	0.6	<0.02
Se	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.1	<0.5	<0.5	<0.5	<0.5	<0.1

Table 2. Cont.

Oxide/ Element	Serpentinite		Talc Schist	Chlorite Schist	Hornblendites			Dolomite Vein		Metabasite		Marble		Gneiss	Mica Schist	Syenite
	KL-4	KL-4C	KL-13	KL-5	KL-1	KL-1D	KL-11	KL-3	KL-3C	KL-2	KL-6	KL-12	KL-12F	KL-10	KL-14	KL-9
Li											28.1					2.8
Te											0.02					<0.02
Ge											<0.1					<0.1
In											0.03					<0.02
B											<20					1
F	146	79	330	30	49	39	49	45	66	75		103		1498	825	156
Cl			<50			<100		<200	<190			<35		<80	<130	<75
Au (ppb)	0.9	1.8	0.7	0.8	9.9	<0.5	<0.5	<0.5	<0.5	<0.5	1.7	<0.5	<0.5	0.9	3.3	1.1
Re											<1					<1
Pd											<10					<10
Pt											<2					<2

LOI—lost on ignition, TOT/C—total carbon, TOT/S—total sulfur. Detection limits are usually as follows; in wt. %: SiO₂ (0.01), Al₂O₃ (0.01), Fe₂O₃ (0.04), MgO (0.01), CaO (0.01), Na₂O (0.01), K₂O (0.01), TiO₂ (0.01), P₂O₅ (0.01), MnO (0.01), C (0.02), S (0.02); in ppm: Cr (~13.7), Ba (1), Ni (0.1), Sc (1), Be (1), Co (0.2), Cs (0.1), Ga (0.5), Hf (0.1), Nb (0.1), Rb (0.1), Sn (1), Sr (0.5), Ta (0.1), Th (0.2), U (0.1), V (8), W (0.5), Zr (0.1), Y (0.1), La (0.1), Ce (0.1), Pr (0.02), Nd (0.3), Sm (0.05), Eu (0.02), Gd (0.05), Tb (0.01), Dy (0.05), Ho (0.02), Er (0.03), Tm (0.01), Yb (0.05), Lu (0.01), Mo (0.1), Cu (0.1), Pb (0.1), Zn (1), As (0.5), Cd (0.1), Sb (0.1), Bi (0.1), Ag (0.1), Hg (0.01), Tl (0.1), Se (0.5), Li (0.1), Te (0.02), Ge (0.1), In (0.02), B (1), F (10); and in ppb: Au (0.5), Re (1), Pd (10), Pt (2).

As was stated in the previous sections, some lithologies from the newly recognized prospect have high vanadium concentrations. Although the V content in serpentinite (54 ppm) and talc schist (73 ppm) is low, the V content in the chlorite schist (463 ppm) and mineralized dolomite vein (270 ppm) is noteworthy. The hornblendites contain between 765 and 2055 ppm V. However, metagabbro and metadiabase, which are usually closely associated with the magmatic V deposits, have low V contents (62–142 ppm V), similar to the country paragneiss (120 ppm) and mica schist (166 ppm). Carbonate rocks lacking mineralization, i.e., barren dolomite vein and marble, contain no detectable V (<8 ppm). The syenite (16 ppm) contains about an order of magnitude lower V than its host-paragneiss. For comparison, the V content of the Fe-Ti-V mineralization-bearing metabasites of the Ślęża Ophiolite is 852 ppm (recalculated from 0.15 wt. % V_2O_5) [57], thus, significantly lower than the content in hornblendites from Kletno, pointing to the importance of the latter as a vanadium source.

Chromium, which is a diagnostic element for ultrabasic-related origin, content in the serpentinite (2004.7–2470.0 ppm in samples from Kletno) is typical of mantle peridotites. Cr content is also high in the talc schist (2449.5 ppm). In the chlorite schist (88.9 ppm) and metagabbro (109.5–115.9 ppm), Cr content is an order of magnitude lower than in the serpentinite, whereas in all hornblendite varieties, as well as in the barren dolomite vein, marble, and paragneiss, Cr content is below the detection limit (<13.7 ppm; recalculated from <0.002 wt. % Cr_2O_3). However, in the mineralized dolomite vein, Cr content (54.7 ppm) is comparable with the chlorite schist. The Cr content of mica schist is relatively high (150.5 ppm), whereas in the syenite it is low (4.5 ppm). Another diagnostic element of ultrabasic-derived origin is nickel. In the serpentinite from the Żmijowiec Rib (1747–1876 ppm), the nickel content is typical of peridotites. A similar concentration was measured in the talc schist (1835 ppm), whereas in the chlorite schist, Ni is an order of magnitude lower (183 ppm). In other mineralized rocks (hornblendites: 62–66 ppm; mineralized dolomite vein: 101 ppm), as well as in the barren dolomite vein (50 ppm), Ni content is two to three times lower than in chlorite schist. The Ni content in the barren metagabbro and metadiabase (146.8–172 ppm) is comparable to that of the mineralized chlorite schist. The marble has the lowest Ni content (<0.1 to 1.1 ppm), while Ni is more abundant in the country paragneiss and mica schist (26–64 ppm). The syenite is also very poor in Ni (3.3 ppm). Copper, silver, and gold concentrations are low in all the rocks studied. However, in the hornblendite sample with the highest Fe, Ti, and V concentrations (KL-1), Cu and Au contents are also elevated (173.7 ppm Cu and 9.9 ppb Au) relative to other samples.

The fluorine contents in the rocks from the new prospect are relatively high, similar to the part of the Kletno deposit where fluorite was mined. Fluorine concentrations are as follows: serpentinite 79–146 ppm, talc schist 330 ppm, chlorite schist 30 ppm, hornblendites 39–49 ppm, dolomite veins 45–66 ppm, metagabbro 75 ppm, marble 103 ppm, syenite 156 ppm, and country mica schist and paragneiss 825 and 1498 ppm F, respectively. In contrast to F, Cl concentrations are low (below detection limits).

The metagabbro sample (KL-2) has a Zr/Nb value of 34.3, the highest among the studied rocks. Hornblendites span a large range of Zr/Nb values (KL-1 = 7.1, KL-1D = 18.6, and epidote hornblendite KL-11 = 20.8). This range also includes the values for the chlorite schist (Zr/Nb = 7.1), talc schist (Zr/Nb = 16.5) and the mineralized dolomite vein (Zr/Nb = 22.9). The country rocks have the lowest Zr/Nb values: mica schist (9.0), paragneiss (4.4) and syenite (3.4). For the remaining samples, the Zr/Nb value could not be calculated because Nb is below the detection limit.

6.2. Stable Isotopes Ratios

The oxygen, carbon and hydrogen isotope ratios are presented in Table 3. The $\delta^{18}O$ values of serpentine from the serpentinite range from 9.4‰ to 9.8‰. A slightly lower value (but within analytical error) was obtained for chlorite from the chlorite schist ($\delta^{18}O = 9.3‰$), which in turn overlaps the upper limit of amphiboles from the mineralization-bearing hornblendite ($\delta^{18}O = 8.8‰$ to 9.3‰) and the barren metagabbro and metadiabase ($\delta^{18}O = 9.1‰$ to 9.2‰). The $\delta^{18}O$ value of calcite from the epidote hornblendite is significantly higher ($\delta^{18}O = 16.0‰$) than that of amphiboles from the

hornblende. The oxygen isotope composition of calcite from the epidote hornblende is between the values of carbonates from the dolomite veins ($\delta^{18}\text{O}$ from 12.8‰ to 13.9‰) and calcite marble ($\delta^{18}\text{O} = 23.2\text{‰}$). The $\delta^{18}\text{O}$ values of the dolomite veins are similar to the comparable dolomite vein from Naławice ($\delta^{18}\text{O} = 13.0\text{‰}$), which crosscuts the serpentinites of the Central-Sudetic Ophiolite.

Table 3. Oxygen, carbon and hydrogen isotope composition of the studied rocks from Kletno, and comparable dolomite vein from Naławice (the Ślęza Ophiolite, Central-Sudetic Ophiolites).

Sample	$\delta^{18}\text{O}$ Silicate (‰)	Mineral	$\delta^{18}\text{O}$ Carbonate (‰)	$\delta^{13}\text{C}$ (‰)	Mineral	δD Bulk (‰) *
Kletno						
Serpentinite						
KL-4	9.8	Serpentine				−60
KL-4C	9.4	Serpentine				−64
Talc schist						
KL-13						−62
Chlorite schist						
KL-5	9.3	Chlorite				−54
Hornblende and epidote hornblende						
KL-1	9.3	Amphibole				−71
KL-1D	8.8	Amphibole				−66
KL-11			16.0	−8.3	Calcite	−71
Dolomite vein						
KL-3			12.8	−7.2	Dolomite	
KL-3C			13.9	−7.7	Dolomite	
Metagabbro and metadiabase						
KL-2	9.2	Amphibole				−73
KL-6	9.1	Amphibole				
Marble						
KL-12			23.2	+0.1	Calcite	
Paragneiss						
KL-10						−79
Mica schist						
KL-14						−62
Syenite						
KL-9						−99
Naławice						
Dolomite vein						
NS-1			13.0	+2.8	Dolomite	

* All δD values are an average from two analyses.

The carbon isotope composition of calcite in the epidote hornblende ($\delta^{13}\text{C} = -8.3\text{‰}$) is similar to the isotopic composition of dolomite veins ($\delta^{13}\text{C}$ from -7.7‰ to -7.2‰), although differs significantly from the carbon isotope composition of calcite marble ($\delta^{13}\text{C} = +0.1\text{‰}$). The $\delta^{13}\text{C}$ values of the dolomite veins and hornblende from Kletno also differ from the Naławice dolomite vein ($\delta^{13}\text{C} = +2.8\text{‰}$).

The hydrogen isotope composition of serpentinite (δD values from -64‰ to -60‰) is nearly identical to the composition of the talc schist ($\delta\text{D} = -62\text{‰}$), and overlaps, within analytical error, with the highest values of the hornblendites (δD values from -71‰ to -66‰). The hydrogen isotope composition of the latter overlaps the isotopic composition of the metagabbro ($\delta\text{D} = -73\text{‰}$), which has slightly higher values than that of the paragneiss ($\delta\text{D} = -79\text{‰}$). However, the hydrogen isotope composition of the syenite ($\delta\text{D} = -99\text{‰}$), occurring within the paragneiss, does not show correlation

with any of the examined samples. In addition, the hydrogen isotope composition of the country mica schist ($\delta D = -62\text{‰}$) is identical to the composition of talc schist, and the isotopic composition of chlorite schist ($\delta D = -54\text{‰}$) is the highest among the samples.

7. Discussion

7.1. Provenance and Evolution of Igneous and Metigneous Rocks

The serpentinite bulk composition is consistent with abyssal peridotites which have undergone an intermediate degree of partial melting prior to serpentinization followed by seafloor weathering, evidenced by a lower $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio relative to a primitive mantle, and extremely low MgO/SiO_2 (Figure 8) (cf., De Hoog et al. [58], and references therein). The calcium to aluminium ratio of serpentinite ($\text{CaO}/\text{Al}_2\text{O}_3$: 0.11–0.12) is lower than for typical modern abyssal peridotites. However, comparable values were reported for some abyssal peridotites subjected to intense serpentinization and moderate seafloor weathering ($\text{CaO}/\text{Al}_2\text{O}_3$ ratio as low as 0.16; calculated using data of Craddock et al. [59]), and also for likely depleted oceanic mantle, subducted to UHP conditions, serpentinized, and now present as relatively slightly weathered, serpentinized harzburgites in the Eastern Alps, containing relics of olivine and orthopyroxene ($\text{CaO}/\text{Al}_2\text{O}_3$ as low as 0.12 [58]). The extremely low $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of serpentinite can be attributed to serpentinization and/or intense seafloor weathering because the introduction of H_2O into peridotite is associated with metasomatic release of Ca [60]. Moreover, the serpentinite likely underwent interaction with sedimentary-derived fluids post-emplacement as it is documented by slightly elevated $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}$ value from 9.4‰ to 9.8‰) compared to $\delta^{18}\text{O}$ values of serpentinites from modern abyssal peridotites ($\delta^{18}\text{O}$ values from 1.9‰ to 5.3‰ [61]), as well as the presence of carbonate veins associated with pentlandite. However, the elevated $\delta^{18}\text{O}$ values can be caused also by serpentinization by seawater at low temperature. The extensive development of schistosity in the serpentinite, in which one of the major dip directions (71/58) is nearly identical to the orientation of schistosity in the country paragneiss (72/55; Figure 4A,B), suggests a common deformation event under metamorphic conditions of both these lithologies. These data suggest the tectonic emplacement of a depleted peridotite rather than intrusion of ultrabasic magma into the Stronie sequence metasediments [5–10]. However, an alternative interpretation of Smulikowski et al. [10], according to which serpentinite from Kletno is an Alpine-type ultrabasic association, emplaced into regionally metamorphosed country rocks, is consistent with our interpretation to some extent. That is, an Alpine-type ultrabasic body can be also derived from the oceanic lithosphere. Moreover, the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of serpentinite from Kletno is similar to some of Alpine ultrabasites as discussed above. However, we did not find any evidence for HP/UHP metamorphism of serpentinite or the rocks in its vicinity. There is also a lack of evidence that sedimentary country rocks were metamorphosed prior to incorporation of the serpentinite because based on the structural data the serpentinite shares at least one tectonometamorphic episode with the country metasediments.

The barren metabasites from Kletno have a similar mineralogy (both the metagabbro and metadiabase contain amphibole, clinozoisite, chlorite, muscovite, titanite and accessory carbonate and relic plagioclase; Table 1), as well as similar oxygen isotope compositions of the rock-forming amphibole (metagabbro $\delta^{18}\text{O} = 9.2\text{‰}$, metadiabase $\delta^{18}\text{O} = 9.1\text{‰}$). The only differences are grain size and texture, thereby suggesting that metagabbro and metadiabase were derived from the same magma source. These metabasites are either due to two magmatic pulses sourced from the same magma chamber, or are different sections of the same intrusion. Importantly, the textures and mineralogical composition of the barren metagabbro and metadiabase from Kletno are similar to those of, in places ophitic, metabasites from the western wing of the OSD, which are composed of amphibole, plagioclase, epidote-zoisite group minerals, titanite, quartz, calcite, chlorite, sericite, and ilmenite [21]. The metabasites from the western limb of the OSD contain zonal amphibole, with an actinolite core and a magnesio-hornblende rim [21]. This amphibole is compositionally similar to that documented in the mineralized hornblendites from Kletno (amphibole with an actinolite core and magnesio-hastingsite or

pargasite rim; Table 1). Magnesio-hornblende is also present in the barren metagabbro from Kletno, which contains less bulk Fe than the hornblendites.

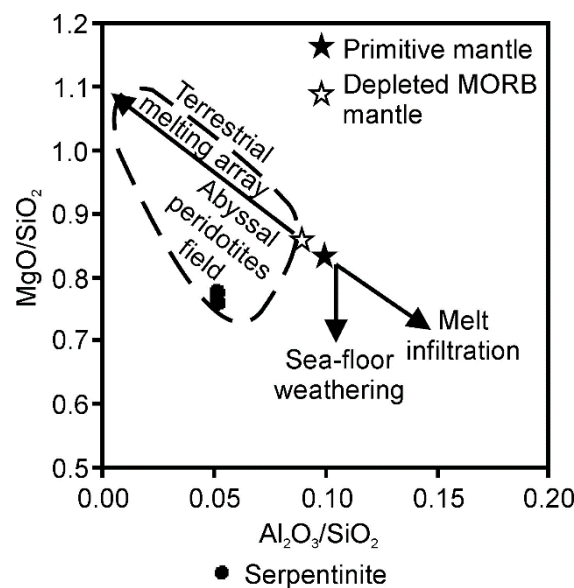


Figure 8. Serpentine bulk-rock composition presented in terms of $\text{Al}_2\text{O}_3/\text{SiO}_2$ vs. MgO/SiO_2 . Diagram for abyssal peridotites based on De Hoog et al. [58], and references therein.

The REE and trace elements patterns of mineralized hornblendites and barren metagabbro from the Kletno deposit are similar (Figure 9A,B), suggesting a common origin. Moreover, the REE and trace element patterns of metabasites from Kletno are similar to the patterns of E-MORB-like tholeiitic and slightly enriched N-MORB-like tholeiitic metadiabases and metabasalts (including pillow metabasalts) from the western limb of the OSD [21]. REE and trace elements contents in some hornblendites from Kletno are similar to the most trace element depleted metabasites of the western wing of the OSD, whereas other hornblendites and the barren metagabbro are characterized by a slightly lower trace element content than metabasites from the western limb of the OSD. However, regardless of the lower content of the measured elements in some samples from the Kletno deposit, plots for these samples are parallel to the plots for metabasites of the western limb of the OSD. The only exceptions are positive Sr anomalies, and positive or negative Eu anomalies in samples from Kletno, which are not observed in the metabasites from the western limb of the OSD. However, enrichment in Sr, and enrichment or depletion in Eu, may be caused by interaction with sedimentary material. Moreover, Zr/Nb values of the barren metagabbro and mineralized hornblendites (Zr/Nb ratios = 7.1 to 34.3), adjacent to the serpentinite, are comparable with values of the variable MORB-like tholeites from the western limb of the OSD (Zr/Nb values span 9 to 27) [21]. Geochemical similarities to MORB-like tholeites link the gabbroic magma source to the mid-ocean ridges, consistent with the interpretation of adjacent serpentinite as an abyssal peridotite remnant. Additionally, metagabbro and hornblendite from Kletno have higher Zr/Nb values and lower REE and trace element concentrations than those of the OIB-like alkaline metadiabase (Zr/Nb = 5 [21]), thus, excluding a within-plate magma source. The OIB-like alkaline metadiabase from the western limb of the OSD is also characterized by an order of magnitude higher LREE, Th, Ta, Nb, Zr, and Hf contents than metabasites from Kletno. Further, it is characterized by a slight negative Sr anomaly, which is in contrary to positive Sr anomalies in most of metabasites from the Kletno deposit. In sum, the mineralogical composition and bulk chemistry of metabasites from the Kletno deposit, are similar to the MORB-like tholeiitic metabasites from the western limb of the OSD, suggesting their genetic relationship.

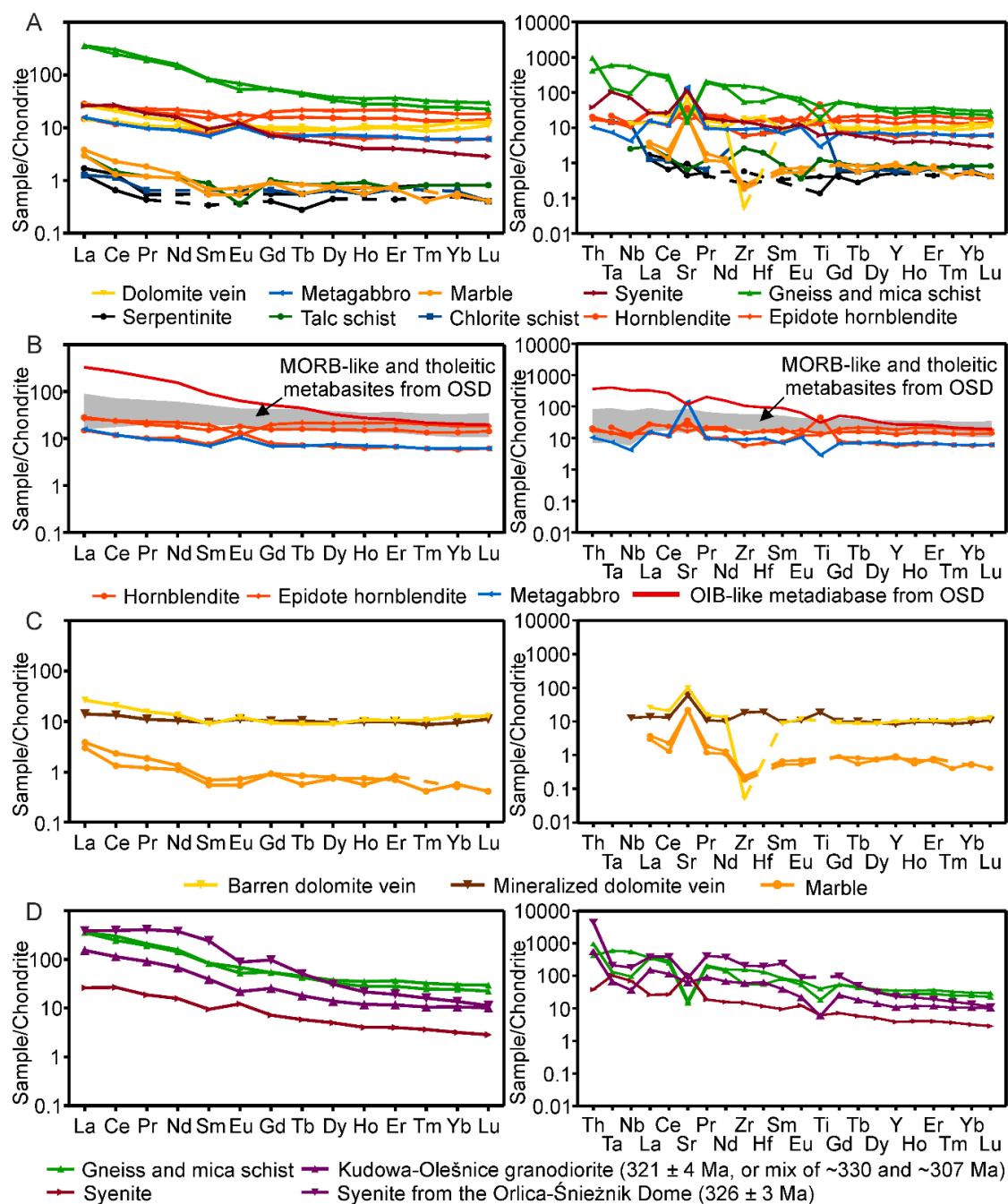


Figure 9. The chondrite-normalized rare earth elements (REE; left hand) and selected trace elements (right hand) patterns of rocks from the Kletno deposit and comparable samples. **(A)** Serpentinite, talc schist, chlorite schist, hornblendites, dolomite veins (without subdivision into barren and mineralization-bearing veins), barren metagabbro, marble, country non-carbonate metasediments (jointly paragneiss and mica schist), and syenite vein hosted in paragneiss; **(B)** Metagabbro and hornblendites plotted against various MORB-like and tholeiitic metadiabases and pillow metabasalts, and OIB-like metadiabase from the western limb of the OSD [21]; **(C)** Dolomite veins (subdivided into the barren dolomite vein and mineralization-bearing vein) plotted against country marble; **(D)** Country paragneiss and mica schist plotted against syenite vein hosted in paragneiss, as well as post-tectonic syenite vein from the western limb of the OSD [41] and granodiorite of the Kudowa-Olešnice massif [35].

The extensive development of schistosity in the serpentinite, in one out of the two major dip direction orientations is nearly identical to the schistosity orientation in the surrounding paragneiss (Figure 4A,B), points to a common tectonothermal event. This tectonothermal event likely took place ca. 340 Ma [23,24], based on structural analyses and U–Pb dating of zircons, especially rims of the zoned zircon grains from the adjacent orthogneisses. Thus, previous interpretations of the Kletno serpentinite as a post-tectonic vein or diatreme cannot be further substantiated. A similar orientation of schistosity in the serpentinite and country paragneiss along with the content of major elements is consistent with the origin of the serpentinite as a fragment of abyssal peridotite (see Figure 8) incorporated into the continental crust and sharing, at least in part, a tectonometamorphic history with the country metasediments. Moreover, the presence of metabasites similar in terms of mineralogical composition, REE and trace elements content and Zr/Nb ratios, to metabasites from the western wing of the OSD coeval with the Stronie sequence deposition [21], in the proximity to the serpentinite from Kletno, suggests serpentinite emplacement earlier than the Stronie sequence deposition proceeded (i.e., before ca. 532 Ma [19]). Consequently, the serpentinite is likely a remnant of the abyssal peridotite or a back-arc basin floor of the Cadomian age, or an effect of Cambrian rifting. The abyssal peridotite was subsequently overlain by the Stronie sequence metasediments protolith, not earlier than ca. 532 Ma. When the Stronie sequence deposition began, the peridotite was likely serpentinized to some extent, due to the interaction with water during the peridotite evolution from a spreading center to exposure at the seafloor, where it was overlain by sediments. During the Stronie sequence deposition, MORB-like gabbro and diabase intruded the seafloor. This triggered metasomatic activity and melt/fluid-rock interactions enabling the crystallization of magnetite near the liquidus in mafic melt, broadly described in the next subsection, and possibly forming talc in the serpentinite. Hence, the serpentinite affinity with the ca. 400 Ma Central-Sudetic Ophiolite, derived from a significantly younger oceanic lithosphere, is unlikely. The REE and trace element characteristics of hornblendites and barren metagabbro are similar (Figure 9A,B), and the only notable difference is a slight negative Eu anomaly in the epidote hornblendite sample, in contrast to slightly positive Eu anomalies in the other hornblendites and metagabbro. Another difference is a negative Ti-anomaly in the metagabbro, contrasting with a positive Ti-anomaly, or lack of any anomaly in the hornblendites, although this is caused by the extensive Fe–Ti–V mineralization in the hornblendites (accumulation of Fe and Ti oxides). Thus, we interpret the hornblendites as metamorphosed ferrogabbros, related to the same basic magma intrusion as the barren metagabbro protolith. In addition, the metagabbro and hornblendite REE and trace element patterns are similar to those of the dolomite veins (Figure 9A,C).

The dolomite veins, especially the mineralized veins, have REE and trace element patterns resembling those of the metagabbro and hornblendites, although they are also similar to marble patterns (Figure 9C). The dolomite veins are characterized by a slight enrichment in LREE relative to MREE and HREE, as well as flat MREE and HREE patterns, and a positive Sr anomaly. These features are typical of the marble from Kletno, although a positive Sr anomaly is typical of both the marble and metagabbro. Highly negative Nb, Zr and Hf anomalies of the barren dolomite vein are also similar to the marble. The REE and trace elements patterns of the barren dolomite vein are parallel to the marble patterns, regardless of higher content of almost all elements (with the exception of Zr) in the barren dolomite vein compared to the marble. These similarities suggest a genetic relationship between dolomite veins and both the gabbroic intrusions and country marbles. The intrusion of the mafic magma into the marble probably caused decarbonation generating CO₂-rich fluids which led to the formation of the dolomite veins. Alternatively, the CO₂-rich fluids, generated from carbonate sediments during extensive metasomatic hydration of the oceanic lithosphere after emplacement of the gabbro, can interact with the gabbro causing its carbonation. Moreover, the mineralization-bearing dolomite vein pattern is similar to that of the metagabbro, whereas the barren dolomite vein is more similar to the marble. Thus, ore-grade of the dolomite veins may depend on the gabbro-derived to marble-derived material ratio. The REE and trace element patterns of metagabbro, hornblendites and dolomite veins differ from those of the paragneiss and mica schist, which have high LREE/HREE

ratios and a negative Sr anomaly. However, the Fe and Ti contents of the mineralization-bearing hornblendites and dolomite vein is similar to that of the paragneiss and mica schist, suggesting an influence, although to a limited degree, of the non-carbonate metasediments for the formation of the mineralization-bearing metabasites and dolomite veins. In addition, the LREE, Zr and Hf contents of the metabasites and dolomite veins are similar as those of the syenite (Figure 9A,D), suggesting a potential limited influence of the syenitic intrusion on the metabasites and dolomite veins formation. This suggests a possibility of a pervasive migmatization in the Orlica-Śnieżnik Dome (ca. 340 Ma [23]), intrusion of the syenite dykes of the western OSD (326 ± 3 Ma [41]), or intrusion of the Kudowa-Oleśnice granitoids (ca. 330 Ma [35,40]) involvement in the evolution of the metabasites and dolomite veins. With these magmatic events, the syenite from Kletno can be linked based on a similar distribution of the REE and trace elements, with the exception of the positive Sr anomaly in syenite (Figure 9D).

The mineralogical composition of the hornblendites and metagabbro, which differs from the magmatic ferrogabbros and barren gabbros, is likely a result of a later metamorphic overprint under greenschist to epidote-amphibolite facies. Retrograde metamorphism resulted in formation of actinolite, pargasite, ferro-pargasite, ferro-sadanagaite, magnesio-hastingsite, epidote-clinozoisite solid-solution, brunsvigite and ripidolite in hornblendites, as well as actinolite, pargasite, magnesio-hornblende, clinozoisite, clinocllore and sheridanite in the metagabbro and metadiabase, and almost complete obliteration of pristine feldspars (except fine labradorite relics in metagabbro; see Table 1 and Table S10) and pyroxenes in these rocks. The metamorphic overprint also affected ore mineralization. For example, in the metagabbro and hornblendites, magmatic ilmenite was replaced by metamorphic titanite and likely secondary ilmenite (Figure 6E). Based on textural features, the metamorphic origin of titanites in both the barren and mineralization-bearing metabasites is consistent with their Fe/Al ratio (cf., Ling et al. [62], and references therein; Figure 10). In contrast, titanite from the syenite plots outside the field of metamorphic titanites pointing to post-metamorphic formation of titanites from the syenite. Thus, the syenite intrusion likely postdates ilmenite alteration to titanite in the metabasites, which in combination with the differences in REE and trace elements contents and patterns between metabasites and dolomite veins, and syenite vein, argues for limited or no influence of the syenite intrusion on formation of Fe-Ti-V mineralization (cf., Figure 9A,B,D). In addition, the differences in chlorite (Figure 7), amphibole, and epidote-group mineral compositions between the metagabbro and hornblendites are likely related to differences in the Fe, as well as the Si and Al contents of these rocks. However, the metamorphic overprint of metabasites may also be associated with fluid-mediated transport, leading to the secondary enrichment of these metabasites in Fe, Ti and V. However, if this is the case, then Fe and Ti introduction associated with a metamorphic reequilibration is limited, and a major source of Fe and Ti is linked with the magmatic episode, as evidenced by a primary, magmatic ilmenite presence in hornblendites (and probably also magmatic magnetite as discussed in the next subsection). Moreover, as discussed above, the barren metagabbro, hornblendites, dolomite veins, and marble REE and trace element patterns show numerous similarities with each other, whereas the REE and trace element patterns of non-carbonate metasediments are more different. Thus, if a broad chemical reequilibration during metamorphism took place, then the gabbros, dolomite veins and marbles interacted each other, whereas chemical exchange between these rocks and non-carbonate metasediments was more limited, and influenced only selected elements (e.g., Fe and Ti). However, based on the bulk compositions, a mafic melt enrichment in Fe and Ti derived from sediments tends to be another factor involved in the formation of magmatic Fe-Ti-V deposits. Moreover, vanadium in the ore-bearing rocks is incorporated in magnetite (average V_2O_3 contents vary between 0.27 and 0.87 wt. % in various mineralized lithologies) and ilmenite (average V_2O_3 contents span 0.30 to 0.48 wt. %), and subordinate in titanite and garnet (both characterized by the average V_2O_3 content of 0.38 wt. %). That, jointly with a secondary origin of titanite, garnet, and some sort of magnetite and ilmenite (e.g., Figure 6E), also suggests a possible vanadium mobilization and exchange with the wall-rock sediments to some extent during metamorphism.

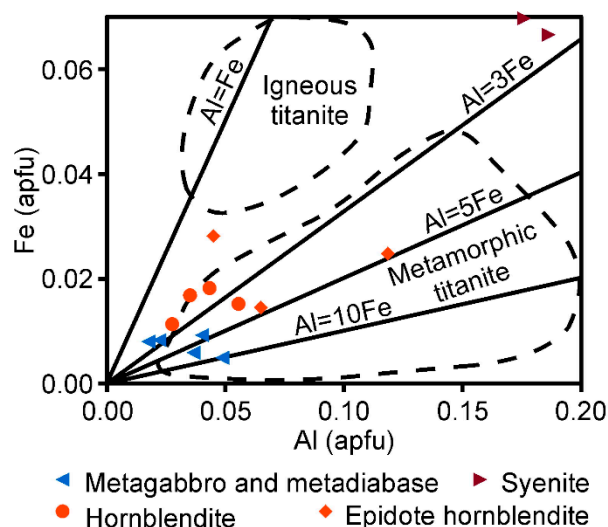


Figure 10. Titanites composition in terms of Al vs. Fe ratio. Discrimination diagram of titanites modified after Ling et al. [62], and references therein.

7.2. Mineralization Origin and the Fluid Source

The oxygen and hydrogen isotope compositions of both the barren metabasites and mineralized hornblendites ($\delta^{18}\text{O}$: 8.8‰ to 9.3‰, δD : −73‰ to −66‰), are similar to the isotopic composition of dolomite-related nephrite (skarn) from the Złoty Stok deposit ($\delta^{18}\text{O}$: 8.3‰ to 10.4‰, δD : −77‰ to −75‰ [31]; Figure 11A). In both cases, the barren metabasites and mineralized hornblendites from Kletno and the nephrite from Złoty Stok, the $\delta^{18}\text{O}$ value was measured on amphibole separates (tremolite in the case of the nephrite) and δD value on the bulk rock samples. Additionally, the oxygen and carbon isotope composition of carbonates from hornblende and dolomite veins from Kletno ($\delta^{18}\text{O}$: 12.8‰ to 16.0‰, $\delta^{13}\text{C}$: −8.3‰ to −7.2‰) plot in the middle of the range of carbonates from the mineralized marbles and skarns from the Złoty Stok deposit ($\delta^{18}\text{O}$: 8.4‰ to 21.1‰, $\delta^{13}\text{C}$: −13.2‰ to −3.0‰; [63]; Figure 11B). The only exception is the oxygen isotope composition of the barren marble from Kletno ($\delta^{18}\text{O}$ = 23.2‰, $\delta^{13}\text{C}$ = +0.1‰), which is higher than that of the barren or slightly serpentinized marbles from Złoty Stok ($\delta^{18}\text{O}$: 13.6‰ to 15.4‰, $\delta^{13}\text{C}$: −2.9‰ to −1.3‰ [63]). However, this minor difference in the isotopic composition of the carbonate wall rock does not influence the isotopic composition of the skarn, which is comparable with the mineralized lithologies from Kletno. Corresponding isotopic compositions of skarn from Złoty Stok (including nephrite) and rocks of the newly recognized ore prospect in Kletno may suggest similarities in the formation mechanism, i.e., similar temperature during formation or equilibrium with fluid of a similar composition. The nephrite (skarn) from the Złoty Stok deposit is interpreted to have formed due to Kłodzko-Złoty Stok granite-derived fluids interaction with country dolomitic marbles of the same Stronie sequence [31]. Although a majority of the intrusive rocks from the Złoty Stok deposit are felsic to intermediate, a mantle-derived magma input was an important factor for their formation, in extreme cases leading to the gabbro and lamprophyre bodies formation [29,34–36]. Therefore, interaction of carbonates with magma-related fluids with a similar composition in both the Kletno and Złoty Stok deposits is probable.

In addition, the oxygen and carbon isotope composition of silicate and carbonate minerals from a distant marble (calcite $\delta^{18}\text{O}$ = 23.2‰, $\delta^{13}\text{C}$ = +0.1‰), as well as both barren and mineralized metagabbro, hornblende, and carbonate vein samples (amphiboles $\delta^{18}\text{O}$: 8.8‰ to 9.3‰, carbonates $\delta^{18}\text{O}$: 12.8‰ to 16.0‰, $\delta^{13}\text{C}$: −8.3‰ to −7.2‰) show isotopic similarity to analogous rocks from the large, magmatic Panzhihua Fe-Ti-V deposit in SW China (Figures 11B and 12). In Panzhihua, the $\delta^{18}\text{O}$ values of carbonate sediments, located away from the mineralized zone, are higher (carbonate $\delta^{18}\text{O}$: 18.6‰ to 28.6‰), whereas the $\delta^{18}\text{O}$ value of gabbro located outside the mineralized zone is lower (plagioclase $\delta^{18}\text{O}$ = 7.4‰), than $\delta^{18}\text{O}$ values of carbonates and silicates from the ore-bearing gabbro and its contact

aureole (plagioclase $\delta^{18}\text{O}$: 8.2‰ to 8.9‰, carbonates $\delta^{18}\text{O}$: 12.9‰ to 21.3‰) [64]. Similarly, the $\delta^{13}\text{C}$ values of carbonates, sampled away from the mineralized zone, are higher ($\delta^{13}\text{C}$: −1.1‰ to +4.7‰, except of a single marl with $\delta^{13}\text{C}$ = −11.8‰) than values of carbonates from the contact aureole of the ore-bearing gabbro in Panzihua ($\delta^{13}\text{C}$: −9.6‰ to +1.3‰). This intermediate isotopic composition between the country carbonate sediments and barren gabbro suggests involvement of both these rocks in the formation of the Fe-Ti-V ore-bearing gabbros, thus the Panzihua deposit was interpreted as an ore-body formed due to mafic magma intrusion into the sedimentary sequence, abundant in limestones, marls and dolomites [64]. The exact mechanism of interaction between gabbroic magma and carbonaceous sediments is unclear but may involve several processes. The proposed ones are an assimilation of the sedimentary host-rock by mafic magma, mixing of this magma with melts originating from the anatexis of sedimentary rocks, or interaction of melts with the CO_2 -rich fluids derived from decarbonation of limestones, dolomites, or marls [64]. Our observations point to the importance of the latter process, i.e., the Fe-Ti-V mineralization-bearing hornblendites are spatially-associated with both mineralization-bearing and barren dolomite veins, which can be precipitated by the CO_2 -rich fluid or be an effect of the gabbro carbonation under the influx of the CO_2 -rich fluid. Moreover, experimental constraints on magnetite saturation in basaltic magma, combined with the redox equilibria calculations, showed that influx of the CO_2 -rich gas phase result in the increase of the equilibrium oxygen fugacity, which allows magnetite crystallization near a liquidus, leading to this mineral accumulation and formation of the Fe-Ti-V deposit [65].

The dolomite veins from Kletno ($\delta^{18}\text{O}$: 12.8‰ to 13.9‰, and $\delta^{13}\text{C}$: −7.7‰ to −7.2‰) show isotopic similarities to listvenitic rocks from the Central Eastern Desert (CED) of Egypt (carbonates $\delta^{18}\text{O}$: 6.4‰ to 10.5‰, and $\delta^{13}\text{C}$: −8.1‰ to −6.8‰) [66]. These listvenitic rocks have been interpreted as a product of ophiolite carbonation due to the influx of a mantle-derived CO_2 -bearing fluids [66]. The similar oxygen isotope composition of dolomite veins from Kletno and a comparable serpentinite-hosted dolomite vein from Naławice in the Ślęza Ophiolite ($\delta^{18}\text{O}$ = 13.0‰) also points to the basite/ultrabasite carbonation as a mechanism of dolomite veins from Kletno formation (Figure 11B). In addition, the isotopic compositions of carbonated serpentinites of the CED shows a mixing trend between the depleted-mantle and sedimentary carbonates [66], thus consistent with our interpretation of rocks from the Kletno deposit origin, in which CO_2 -bearing fluids causing carbonation originated from the carbonate sediments due to the influx of the mantle-derived gabbroic magma intrusion. Although REE and trace element patterns of hornblendites and the mineralized dolomite vein differ from those of the paragneiss and mica schist (Figure 9A), similarities in their Fe and Ti contents suggest some genetic links. It is plausible that exceptional Fe and Ti contents in the mineralization-bearing rocks (10.18–20.12 wt. % Fe_2O_3 , 0.91–3.42 wt. % TiO_2) are related to interaction of the mafic magma with fluids, derived from protoliths of the country paragneiss and mica schist (11.76–12.30 wt. % Fe_2O_3 , 1.33–2.95 wt. % TiO_2). However, this preliminary conclusion needs to be tested at more magmatic Fe-Ti-V deposits hosted in mafic rocks.

Application of the deposit-type classification scheme of Dupuis and Beaudoin [67] to the examined rocks from Kletno shows that, despite the high Cu content of one hornblendite sample (KL-1 = 173.7 ppm Cu) and magmatic origin of its protolith, the examined prospect does not correspond with the magmatic Ni-Cu massive sulfide deposit-type (Figure 13A), which is consistent with the low Ni content of hornblendites (62–66 ppm Ni). Magnetite from hornblendites classify it as high temperature magmatic Fe-Ti and V deposits (Figure 13B,C), similar to the case of the Fe-Ti-V mineralization hosted in the metabasites of the Ślęza Ophiolite [17]. In addition, Fe-Ti-V mineralization hosted in dolomite veins also plots in the field of magmatic Fe-Ti, V deposits (Figure 13B,C). Mineralization in the chlorite schist plots near the Fe-Ti, V deposits field, although in the Kiruna-type apatite-magnetite and porphyry Cu deposit fields (Figure 13B,C). However, these deposit types are ruled out due to lack of apatite and elevated Cu content in the chlorite schist. Hence, mineralization in the chlorite schist may also be linked to the magmatic Fe-Ti, V mineralization in nearby hornblendite. The composition of magnetite in the chlorite schist may be explained by chlorite schist formation in the way of ferrogabbro chloritization

in the seafloor setting (at the contact with serpentinite), similarly to that documented in the oceanic core complexes for barren gabbro-serpentinite assemblages [68]. That is, ferrogabbro may be hydrated similarly to the barren metagabbro.

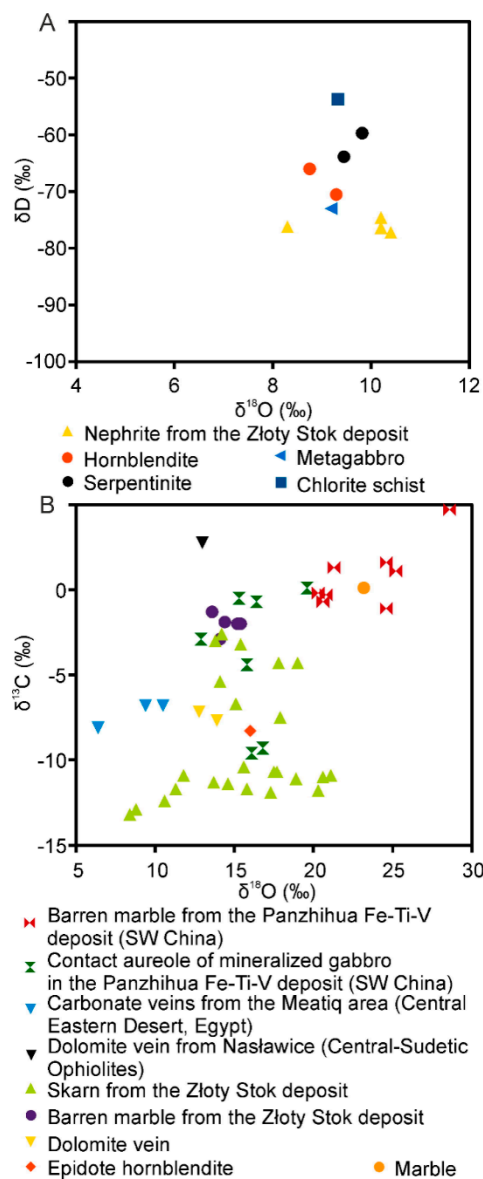


Figure 11. (A) The oxygen isotope composition ($\delta^{18}\text{O}$) of silicate minerals separates vs. hydrogen isotope composition (δD) of bulk-rock samples. A nephrite from the Złoty Stok deposit, formed in the way of dolomitic marble replacement under the influence of granite-derived fluids, is presented after Gil et al. [31]; (B) The oxygen ($\delta^{18}\text{O}$) vs. carbon ($\delta^{13}\text{C}$) isotope composition of carbonates. The barren and mineralized marbles, and skarns from the Złoty Stok deposit, are presented after Mikulski and Speczik [63], the Panzhihua Fe-Ti-V deposit (SW China) after Ganino et al. [64], and carbonate veins within serpentinites of the Central Eastern Desert (Egypt) after Boskabadi et al. [66].

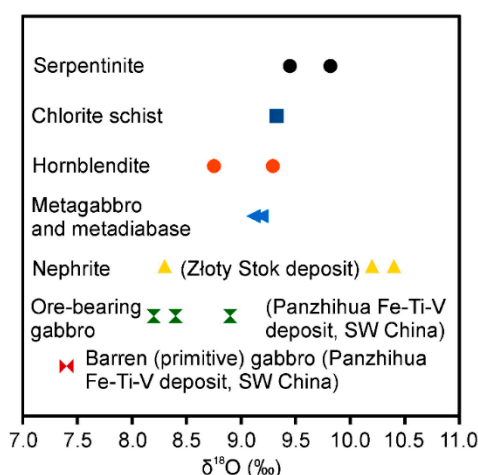


Figure 12. The oxygen isotope composition ($\delta^{18}\text{O}$) of silicate minerals separates. The dolomitic marble-hosted nephrite from the Złoty Stok deposit is presented after Gil et al. [31] and the Panzhihua Fe-Ti-V deposit after Ganino et al. [64].

The talc schist has REE and trace elements contents and patterns (Figure 9A) similar to the serpentinite, as well as the marble. However, the Zr and Hf concentrations are higher in the talc schist and the talc schist lacks the positive Sr anomaly of the marble. Moreover, the Cr and Ni contents in talc schist (2449.5 ppm and 1835 ppm, respectively) are similar as in the serpentinite (2004.7–2470 ppm Cr, 1747–1876 ppm Ni) and much higher than in marble (<13.7 ppm Cr, <0.1 to 1.1 ppm Ni), thus pointing to talc schist formation at the expense of serpentinite. Furthermore, the formation of talc bodies within the recent oceanic lithosphere is interpreted as a result of the Si-rich fluids, related with the later gabbroic intrusions, interaction with an already serpentinitized residual peridotites [61]. On the other hand, talc rocks in modern seafloor settings, especially oceanic core complexes, are formed due to the juxtaposition of serpentinitized peridotites with gabbros at detachment faults, and extensive metasomatic hydration reaction, which enables Si introduction from gabbro to serpentinite [68]. This scenario for the rocks from Kletno is supported by spatial relations, i.e., loose blocks of the talc schist are common in the intimate vicinity of chlorite schist exposures, while the chlorite schist can form at the expense of gabbro. Thus, in the case of the Kletno deposit, talc bodies can be formed due to the infiltration of fluids originating from gabbroic melts intruding serpentinites, or due to later (i.e., postdating gabbro emplacement) extensive metasomatic hydration at the contact of gabbro and serpentinite. The latter reaction may be enhanced by detachment faulting. However, the subsequent intrusion of the more distant Śnieżnik and Gierałtów orthogneisses protolith (ca. 500 Ma [23]), as well as nearby ca. 340–330 Ma syenites intrusion, coeval with the pervasive migmatization of country rocks, also cannot be completely ruled out as a potential Si-rich fluid source. Nevertheless, we postulate, that talc forming Si-rich fluids were more likely derived from gabbros, given that the REE and trace element patterns of the talc schist (e.g., slightly negative slope in LREE and flat HREE, negative Eu anomaly) are more similar to the metagabbro and hornblendite patterns (also slightly negative slope in LREE and flat HREE, positive or negative Eu anomaly), rather than syenite pattern (slightly negative slopes in both LREE and HREE, positive Eu anomaly; Figure 9A). Moreover, the composition of chlorite in the talc schist (penninite) is more similar to chlorite from the barren metagabbro (clinochlore–scheridanite), rather than chlorite from syenite (brunsvigite–ripidolite), i.e., the chlorite in the talc schist is Fe-poor, similar to the metagabbro, which contrasts with the Fe-rich chlorite from syenite (Figure 7). Furthermore, the Śnieżnik orthogneiss is located further from the examined rocks, and hence is also an unlikely fluid source.

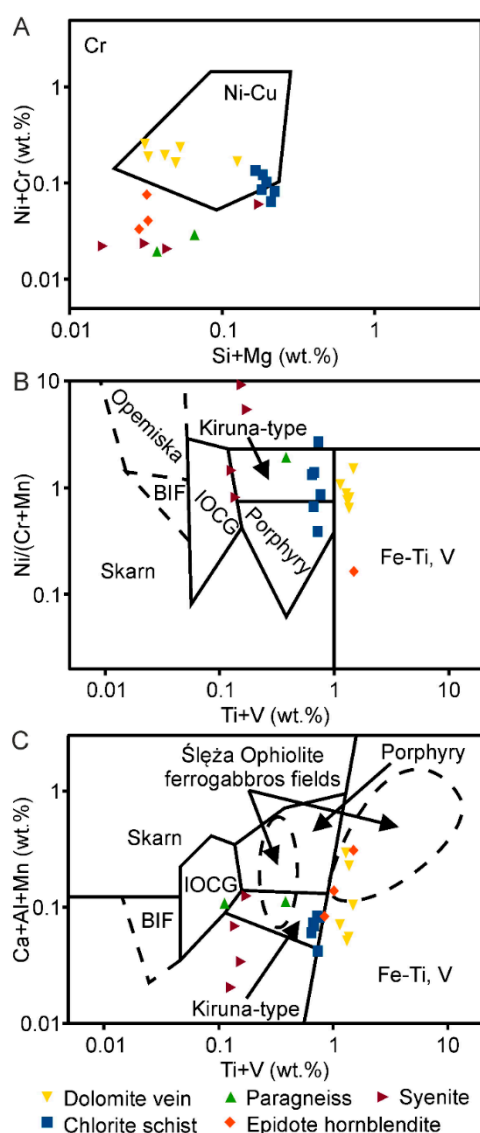


Figure 13. Discrimination diagrams of various types of deposits, based on the composition of magnetite from an ore body. Diagrams modified after Dupuis and Beaudoin [67]; magnetites from country rocks are shown for comparison. (A) Si + Mg vs. Ni + Cr diagram for discrimination of the Ni-Cu-PGE magmatic massive sulfides and Cr deposits of podiform chromite-type; (B) Ti + V vs. Ni/(Cr + Mn) diagram for discrimination of the Fe-Cu skarns, Archean Opemiska-type Cu veins, banded iron formation (BIF), iron oxide-copper-gold (IOCG), Kiruna-type apatite-magnetite, Archean Au-Cu porphyry, and magmatic Fe-Ti and V deposits (ferrogabbros); (C) Ti + V vs. Ca + Al + Mn diagram for discrimination of the Fe-Cu skarns, banded iron formation (BIF), iron oxide-copper-gold (IOCG), Kiruna-type apatite-magnetite, Archean Au-Cu porphyry, and magmatic Fe-Ti and V deposits (ferrogabbros). For comparison, fields of the magmatic Fe-Ti (and V) deposits, hosted in metabasites (ferrogabbro-ferrobasalt) of the Ślęza Ophiolite (the Central-Sudetic Ophiolite) are presented after Wojtulek et al. [17].

In the Kletno deposit, the Si-rich fluids interaction with serpentinites, leading to the talc schist formation, probably took place at low-pressure mid-amphibolite facies conditions, which can be inferred from the occurrence of talc-tremolite-anthophyllite paragenesis in the examined talc schist. According to Boskabadi et al. [66], and references therein, the talc-tremolite-anthophyllite assemblage is stable at the low pressure (<0.2 GPa) mid-amphibolite facies, although it can also be stable due to a higher $\text{SiO}_2\text{-H}_2\text{O}$ activity in the fluid, related with its carbonate-poor nature. The latter explanation is unlike in the case of the Kletno deposit, where talc schist occurs in the intimate proximity of

dolomite veins and carbonate-bearing serpentinite and hornblendites, and not far from marble bodies. The inferred low-pressure mid-amphibolite facies conditions for the talc schist formation are consistent with the hot hydrothermal fluid infiltration at relatively shallow depths in the lithosphere, i.e., the fluid activity near the seafloor. This scenario could have taken place within the Cadomian back-arc basin floor or an oceanic lithosphere, related with an early Cambrian rifting. However, this scenario is in contradiction with provenance of the Stronie sequence, inferred to have originated from the protolith, accumulated in a shallow marine basin [14,18].

8. Summary

Our study shows that the serpentinite from the Żmijowiec Rib was a tectonic slice of abyssal peridotite, subjected to pervasive low-to medium-grade metamorphism and folding, jointly with its country rocks. The hornblendite and dolomite veins are spatially associated with serpentinite, from which they are separated by talc and chlorite schist. The hornblendite, dolomite veins and chlorite schist host Fe-Ti-V mineralization, mostly of magmatic origin. The high V concentrations in the mineralization-bearing rocks is noteworthy. In addition to previously described ore-bearing minerals in the Kletno deposit, we also documented the presence of chromite, ilmenite, rutile, pentlandite, nickeline, zircon, and allanite.

We interpret the hornblendites as a metamorphosed ferrogabbros. The REE and trace element patterns, as well as H and O isotope ratios of the mineralization-bearing hornblendites are similar to those of adjacent barren metabasites, suggesting mineralization-bearing hornblendites and barren metabasite protoliths derivation from a single mafic magma source. This magma source, by comparison with the metabasites from the western limb of the OSD, can be linked with Cadomian MORB-like melts. Moreover, the talc schist was likely a product of serpentinite alteration by Si-rich fluids, derived from the same basic rocks. However, it is not clear whether the serpentinite was transformed to talc under the influence of fluids derived from mafic melt during its emplacement (active intrusion), or as an effect of metasomatic hydration after juxtaposition with solidified gabbro or diabase along a detachment fault.

The oxygen and carbon isotope compositions of the metagabbro, hornblendites, and marble from Kletno corresponds well with isotopic ratios, reported by Ganino et al. [64], for the Panzhihua deposit in SW China, which likely formed as a result of gabbro intrusion into a carbonate-rich sedimentary sequence. The CO₂-rich phase from decarbonation of limestones interacts with the gabbroic melt increasing the equilibrium oxygen fugacity in the mafic magma, allowing magnetite crystallization near the liquidus, and hence causing the accumulation of oxides and formation of the magmatic Fe-Ti-V deposit [65]. This scenario can also explain the newly discovered prospect of Kletno deposit formation, in which the gabbro and diabase were emplaced in the rock sequence, mostly of sedimentary origin, in which limestones are common. The CO₂-rich fluids sourced from limestones decarbonation, regardless of whether of the influx of intruding gabbro or the influx of later, gabbro-derived fluids, likely caused the subsequent carbonation of gabbro and serpentinite.

Summing up, we interpret joint the occurrence of the Fe-Ti-V mineralization in metamorphosed ferrogabbros, as well as ornamental- to gem-quality talc and Fe-Ti-V-bearing dolomite veins, as an effect of mafic intrusion into serpentinites overlain by carbonate-rich sediments, probably in the seafloor setting (Figure 14). In brief, mafic intrusion caused the decarbonation of limestones and release of the CO₂-rich fluids, which reacted with the same mafic magma, allowing Fe-Ti-V oxides crystallization and accumulation (Figure 14). The SiO₂-rich fluids, released from mafic melt during intrusion emplacement, or from gabbro during metasomatic hydration after post-intrusive juxtaposition with serpentinite, caused serpentinite transformation into talc. On the other hand, the CO₂-rich fluids, released from limestones during decarbonation caused by gabbro intrusion, or released from the same limestones during post-intrusive extensive metasomatic hydration, caused gabbro (including ferrogabbro) carbonation and the formation of dolomite. Moreover, Fe- and Ti-bearing fluids derived

from the wall-rock non-carbonate sediments, can cause additional enrichment of the hornblendites, chlorite schists, and dolomite veins in Fe and Ti.

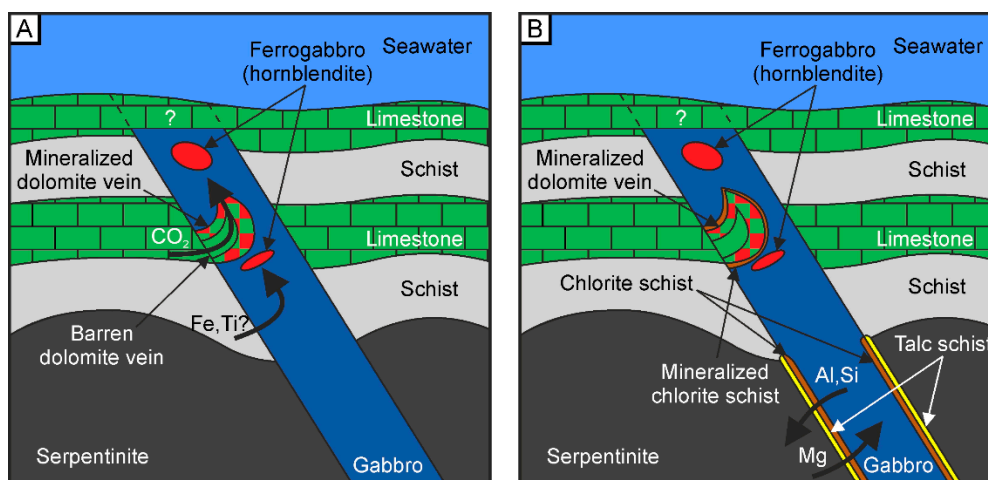


Figure 14. Schematic model of joint Fe-Ti-V mineralization, talc and chlorite schist formation, and carbonation in the fossil seafloor, now present as the ore prospect at the culmination of the Żmijowiec Rib near Kletno. **(A)** The gabbro or diabase intrusion into the serpentinite and its sedimentary cover, composed of limestone and schist. The CO_2 -bearing fluids from the limestone, and probably also Fe- and Ti-bearing fluids from the schist, caused enrichment of the mafic melt in these compounds. The CO_2 introduction caused oxides crystallization and accumulation in the form of ferrogabbro (now present as hornblende). The CO_2 -rich fluids caused gabbro and ferrogabbro carbonation leading to the dolomite veins formation; **(B)** A syn-intrusive or post-emplacement, extensive hydration in the seafloor environment involving both the gabbro (diabase) and serpentinite (possibly also sedimentary cover), which marginal zones were transformed into the chlorite schist and talc schist, respectively. The latter is now present as ornamental talc occurrence. Si and Al were derived from gabbro (diabase), whereas Mg from serpentinite (and possibly also carbonate sediments). Thick arrows indicate source and migration of Si, Al, Mg, Fe, Ti and CO_2 .

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/1/13/s1>, Table S1: Schistosity orientation in serpentinite, chlorite schist and country rock (paragneiss) (the Kletno deposit, Stronie sequence), Table S2: Electron microprobe analyses of serpentine-group minerals from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S3: Electron microprobe analyses of carbonates from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S4: Electron microprobe analyses of talc from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S5: Electron microprobe analyses of chlorites from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S6: Electron microprobe analyses of sulfides from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S7: Electron microprobe analyses of saponite from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S8: Electron microprobe analyses of apatite from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S9: Electron microprobe analyses of muscovite and biotite (micas) from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S10: Electron microprobe analyses of feldspars from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S11: Electron microprobe analyses of the spinel-group minerals from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S12: Electron microprobe analyses of amphiboles from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S13: Electron microprobe analyses of clinopyroxene from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S14: Electron microprobe analyses of garnet from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S15: Electron microprobe analyses of titanite from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S16: Electron microprobe analyses of ilmenite and rutile from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S17: Electron microprobe analyses of zircon from the Żmijowiec rib (the Kletno deposit, Stronie sequence), Table S18: Electron microprobe analyses of epidote-group minerals from the Żmijowiec rib (the Kletno deposit, Stronie sequence).

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