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PERSPECTIVE OF Sn DEPOSIT IN STARA KAMIENICA RANGE W-PART

ANALIZA ZŁÓŻ CYNY W ZACHODNIM REJONIE STAREJ KAMIENICY

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DECLARATION

Hereby, I declare that there is no result in this thesis that has been proposed to obtain an academic degree from university. There is no result or idea that has been reported or published by another author except those cited in this thesis and written in the references.

Krakow, September 2021

Ibnu Munzir

To the persons I love,

My angels, M. Hasbi and Nur Qalbi

My brothers, Capung and Uppy

FOREWORD

This study was fully facilitated by the Economic Geology Department of Geology, Geophysics and Environmental Protection Faculty, AGH University of Science and study was fully conducted. The Department also gave permission, facilitated and assisted the field works and collection and analysis of the sample.

I would like to express my deepest gratitude to my extraordinary supervisor Prof. dr hab. inż. Adam Piestrzyński for his continued guidance, advice, encouragement and support during the study. Also, for all of the lecturers and staffs in Economic Geology Department, the study would never been accomplished without their guidance, suggestion, help and cooperation of numerous persons.

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Last but not least, many thanks addressed to my brothers and sister, Jeremy, Ortu, Afwan and Sherly for their support and kindness to make my master degree so colorful in Poland.

Abstract

The observation of the tin mineralization in Stara Kamienica Range was indicated as Sn-Polymetalic Sulphide Type where some of precious metal such as Co, Ni, Cu, Zn, Pb, Bi, As, Sb and In are also occurred in the area. Investigation is conducted in western part of Stara Kamienica Schist belt as a part of Sudety mountain which situated in Southwestern part of Poland. There were tin and cobalt mine around the area as an indication of mining activity in the past but all of the mines have been closed because of the low-grade concentration of both of the element in the mines. The study is conducted to identify the deposit type of the tin in the study area. During the microscopic observation, presence of Garnet, Tourmaline and Zirconium show an assumption of the different deposit type. Chemical analysis provides an occurrence of rare earth mineral and higher amount of tin and tungsten. Further, the Wavelength-dispersive Spectroscopy (WDS) revealed that most of the Garnet and Tourmaline in the area are mostly almandine and olenite respectively.

Abstract

W pracy wykonano obserwacje i badania mineralizacji cyny w paśmie Starej Kamienicy. Okruszcowanie jest zdominowane przez proste siarczki, w których przeważają niektóre metale jak: Co, Ni, Cu, Zn. W obszarze występują również Pb, Bi, As, Sb i In. Dochodzenie prowadzone jest w zachodnim fragmencie pasa łupków Starej Kamienicy jako część Sudetów leżących w południowo-zachodniej Polsce. W okolicy znajdowała się kopalnia cyny i kobaltu, co wskazuje na działalność górniczą w przeszłości, ale wszystkie obiekty zostały zamknięte z powodu niskiego stężenia obu pierwiastków. Badania były prowadzone, aby rozpoznać typ genetyczny złoża cyny na badanym obszarze. Podczas mikroskopowych obserwacji stwierdzono obecność granatu, turmalinu i cyrkonu, co świadczy o innym rodzaju genezy. Analiza chemiczna wykazała występowanie minerału ziem rzadkich oraz większą ilość cyny i wolframu. Ponadto, spektroskopia z dyspersją fal (WDS) ujawniła, że duży odsetek granatów i turmalinów w okolicy to w większości odpowiednio almandyn i olenit.

CONTENTS

CHAPTER I

INTRODUCTION

1. Introduction

Tin was one of the first metals discovered by humans. Because of the hardening effects on copper, it was utilized in bronze objects as early as 3500 B.C. The copper-tin alloy combination was used for sharpening and was hard enough to retain a cutting edge, and it was utilized to make construction equipment, household items, and weaponry. The majority of tin today is used as a protective coating or in alloys with other metals. Tin is utilized in a variety of applications, including steel can coatings, electronic solders, pipe welding, electrical conductors, bearings, and other alloys. Tin is crucial to an industrial society and is used in a variety of applications where it cannot be replaced.

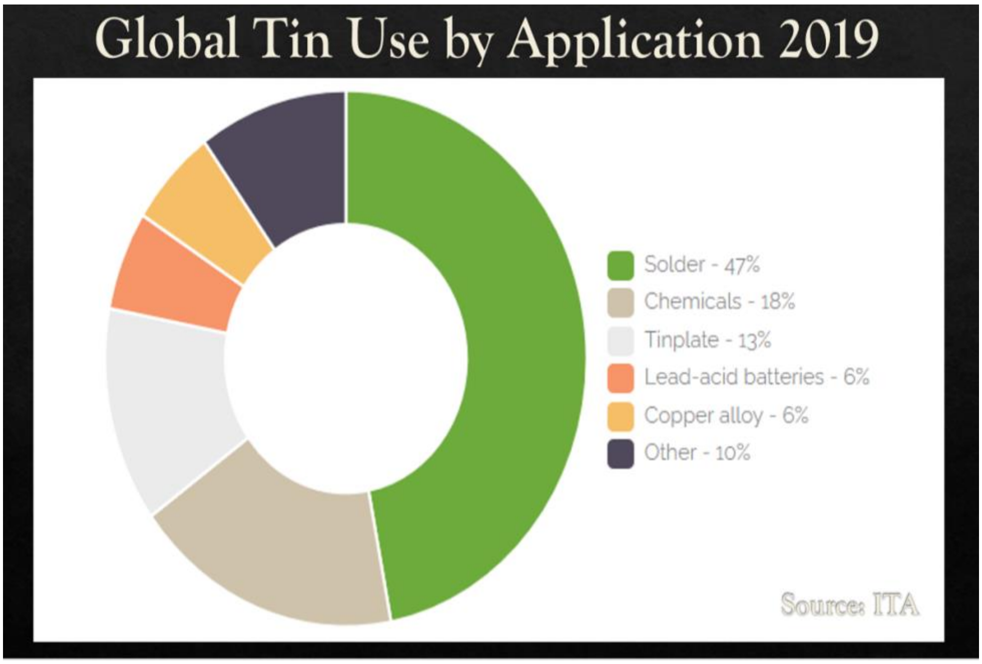


Fig 1. Tin use during technological improvement in 2019 (ITA, 2020)

Tin demand is expected to rise considerably in the future as technology improves, with this element being the most impacted element in use. Finding a new economic tin deposit to meet demand is the best way to provide a benefit as an income to the country in relation to national income. Tin, a precious metal that has been mined for human purposes since the Bronze Age, has a long history of exploration and mining. As a result, three-dimensional studies have been conducted on a number of key mining regions. The geology of tin deposits is rather well known compared to that of many other metals, and even though new producing regions are being discovered, the geology of each new prospected area have been documented in scientific works as the summarize of the tin reserve in the future.

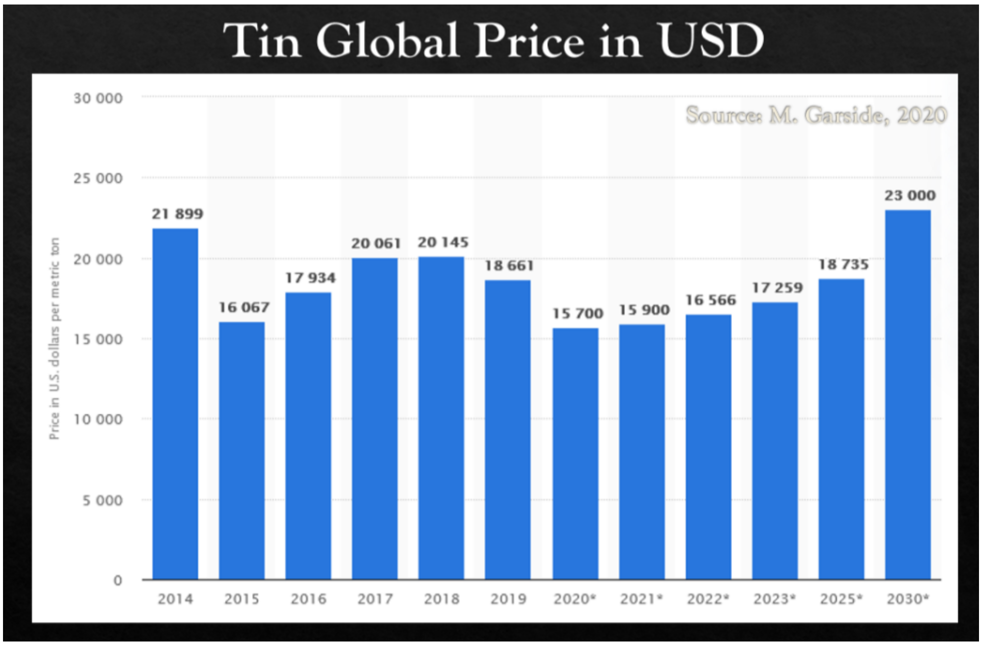


Fig 2. Tin price forecast (Garside, 2020 in statista.com)

Many other important metals are recovered during the mining and concentration of tin ores, including the majority of commercial tin, which is smelted from concentrates containing a high proportion of tin in cassiterite. Tantalum, niobium, tungsten, copper, lead, zinc, silver, arsenic, and antimony are all important metals found in lode deposits; others may provide beryllium in the future. Niobium, tantalum, and rare-earth minerals are abundant in placer deposits. Biotite or biotite-muscovite granite in Bolivia, shallow-deposited in ted volcanic rocks such as quartz latite or dacite, are almost associated with significant tin deposits. Tin granites are granites that have tin deposits connected with them.

Tin deposits are the best example of epigenetic magmatic ore deposits as a whole. Most of the world's major lode areas are either (1) long, narrow belts of tin-bearing granites within a larger intrusive complex (Southeast Asia), or (2) more widespread bands of newer granites within large areas of Precambrian rocks (Nigeria). The majority of the large linear bands run along continental borders or major orogenic belts inland, where granite magma was formed. Some are linked to tectonic activity along portions of broad transcurrent faults, which represent the continuation beneath continents of significant cracks impacting ocean basin subcrustal rocks (Siberia). Most tin deposits are documented along the tectonic belts which related to intruded granite, and their ages is dated from Precambrian to Tertiary, while some researchers (Pereira and Dixon, 1971) believe that statistical studies demonstrate that tin deposits are more abundant in younger rocks.

The tin occurrence in Poland are identified in several different places in South-western part, especially in Stara Kamienica Schist Belt which also constitute with Karkonosze granite.

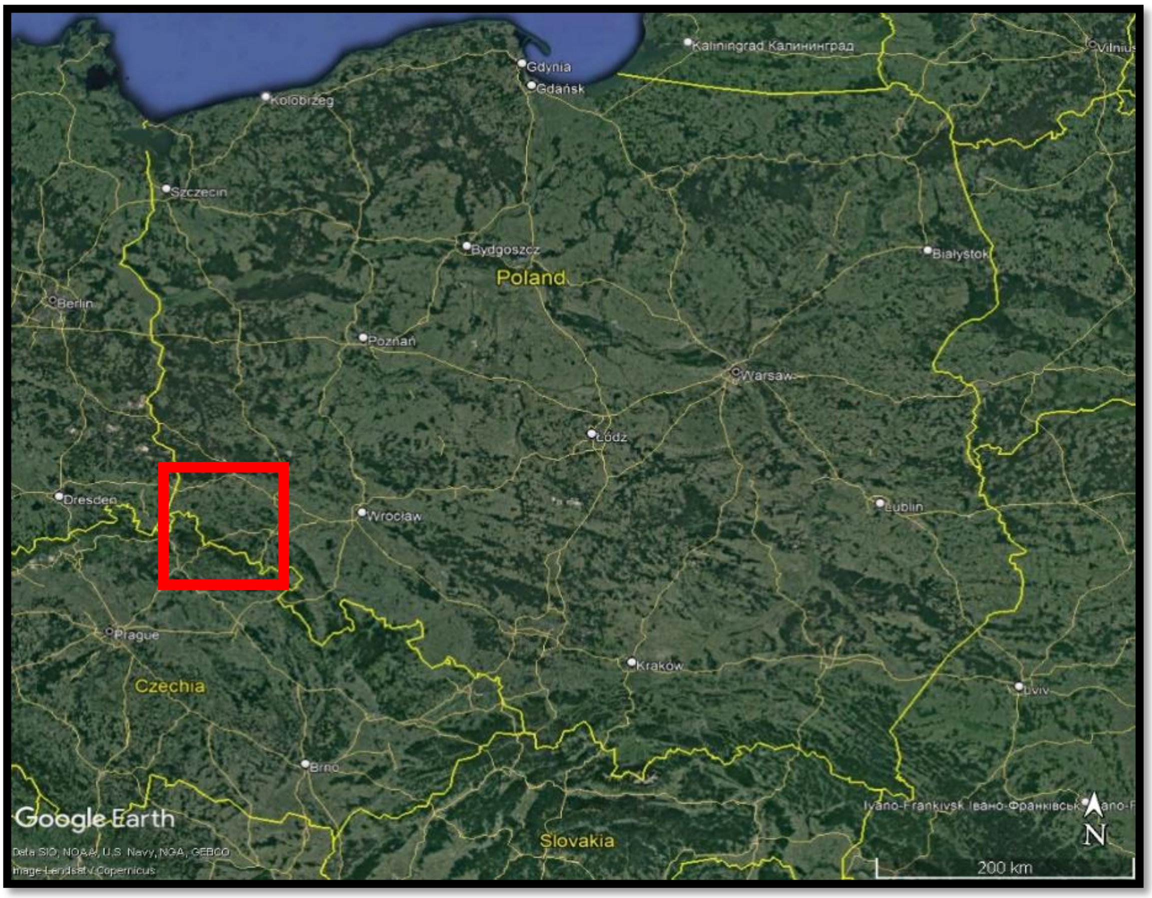


Fig 3. Study area location in Southwestern part of Poland (Google Earth, 2021)

Krobica and Gierczyn region are well-known as the place where the deposit was identified. Some works about tin deposit have been conducted in the area which resulted more speculation about the deposit type and the origin of the deposit. This work is aimed to determine the deposit type including the origin and their ore mineralization of the tin deposit in Stara Kamienica Range, specifically in the western part.

CHAPTER II

GEOLOGICAL SETTING

3.3 Geology of Stara Kamienica Schist Belt

The Karkonosze– Izera Massif, which passes westward into the Lusatian Massif and is almost fully inside German territory, is the largest geological block in the western part of the Sudetes. The massif includes the Izera Mountains and the Karkonosze, which constitute a morphological axis for the Western Sudetes. The highest peak in the Izera Mountains, Wysoka Kopa, is 1126 meters above sea level, while the highest point in the Karkonosze and the Sudetes is Śnieżka (1602 m a.s.l.). The Wysoki Grzbiet ridge, cut off on the south by the Izera River valley, and the Grzbiet Kamienicki ridge, divided by the Kwisa River valley, form the Polish portion of the Izera Mountains, both oriented WNW–ESE. To the north, the Izera Mountains descend into the Izera Foothills, a hilly region with an average elevation of 470–350 meters above sea level. The Polish Karkonosze stretches from the Szklarska Pass in the west to the Lubawka Gate in the east, with a WNW–ESE direction. They are shut off from the Jelenia Góra Valley to the north by a steep topographical edge that runs between Piechowice and Kowary, separating the Karkonosze from the Jelenia Góra Valley. To the west, a zone of NNE–SSW-trending ytawa–Zgorzelec depressions flled with Cenozoic deposits separates the Karkonosze–Izera Massif from the Lusatian Massif. To the east, it is bounded by the Intra-Sudetic Trough, while to the north, it is connected to the Kaczawa Structure by a complicated zone of the so-called Main Intra-Sudetic Fault. The Karkonosze–Izera Massif's geological development is closely linked to about 200 million years of plutonic granitic activity. (Cwojdziński, Pacuła, 2013).

The Izera Mountains and Foothills are part of the Izera Metamorphic Complex, and they can be found in the area ranging from Wieradów-Zdrój to Jelenia Góra. These are orthogneisses that originated 500 million years ago as granites intruding into an aureole represented now by four longitudinal schist belts of mica-chlorite schists. According to Wiszniewska (1982), there are four distinguished petrographic types of schist in the Stara Kamienica Schist Belt:

1. Quart-Muscovite-Schist
2. Quartz-Muscovite-Biotite-Schist
3. Quartz-Muscovite-Biotite-Chlorite-Schist
4. Quartz-Muscovite-Biotite-Chlorite-Garnet-Schist

The Wysoki Grzbiet (Szklarska Poreba) belt, which has been thermally metamorphosed along the contact with the Karkonosze granites, the Stara Kamienica belt, which is best known for tin (cassiterite) and cobalt mineralization, the narrow and discontinuous Gieratówek–Mirsk belt, and the Zotnickie (Zotniki Lubaskie) belt are all The schist belts all occur inside a zone of major orthogneisses in the middle section of the Karkonosze–Izera Block, and their arcuate form, apparent in the geological map, emphasizes this arrangement of structural metamorphic features.

The schists of the belts originated more than 600 million years ago as a result of metamorphism of sedimentary rocks such as claystones and sandstones during the Neoproterozoic, possibly transitioning to the Early Cambrian. It is currently unknown whether they are pieces of the upper (top) or lower (basal) aureole of the Izera granites' original intrusion. Elongated outcrops of light-colored albit-enriched leucogranites with intercalations of tourmaline quartzites (Stara Kamienica belt, Zotnickie belt) mark the boundary between the schist complex and the neighboring gneiss complex to the south.

Primary granites underwent severe mylonitic deformation, resulting in the creation of the Izera orthogneisses. In the form of layered, augen, and lenticular structures, the method has produced a distinctive directional fabric. There are portions of the gneisses with intact non-directional texture that seem like coarse- or medium-grained granites made up of feldspars (plagioclase and microcline), quartz, biotite, and muscovite. They're primary granite shards that aren't too deformed or aren't too deformed. The Izera rocks went through a mylonitization process 400–340 million years ago (from the early Middle Devonian to Early Carboniferous) with the entire orthogneiss-schist complex, there are also inserts of amphibolites, as well as diabase, lamprophyre and quartz veins.

3.4 Geology of Stara Kamienica tin deposit

Karkonosze-Izera In Central Europe, the Metamorphic Block is found in the southwestern section of Poland. The principal rock complexes in the region are five parallel schist belts separated by gneisses and the Variscan Karkonosze granitoid massif. The samples used in this study come from the Stara Kamienica Range (SKR) schist belt, which contains gneisses, quartz veins, schists, leucogranites, and greisens, among other rock types. The mica schist band stretches for about 27 kilometers from west to east, with an average width of one kilometer. From south to north, the schist belt dips 500 to 700 meters. The rocks are Precambrian metapelites that were regionally metamorphosed by Variscan metamorphism to a quartz-epidote-almandine subfacies of greenstone facies

(Winkler, 1967). The metamorphism process is thought to have occurred between 310 and 320 Ma (Borkowska et al., 1980).

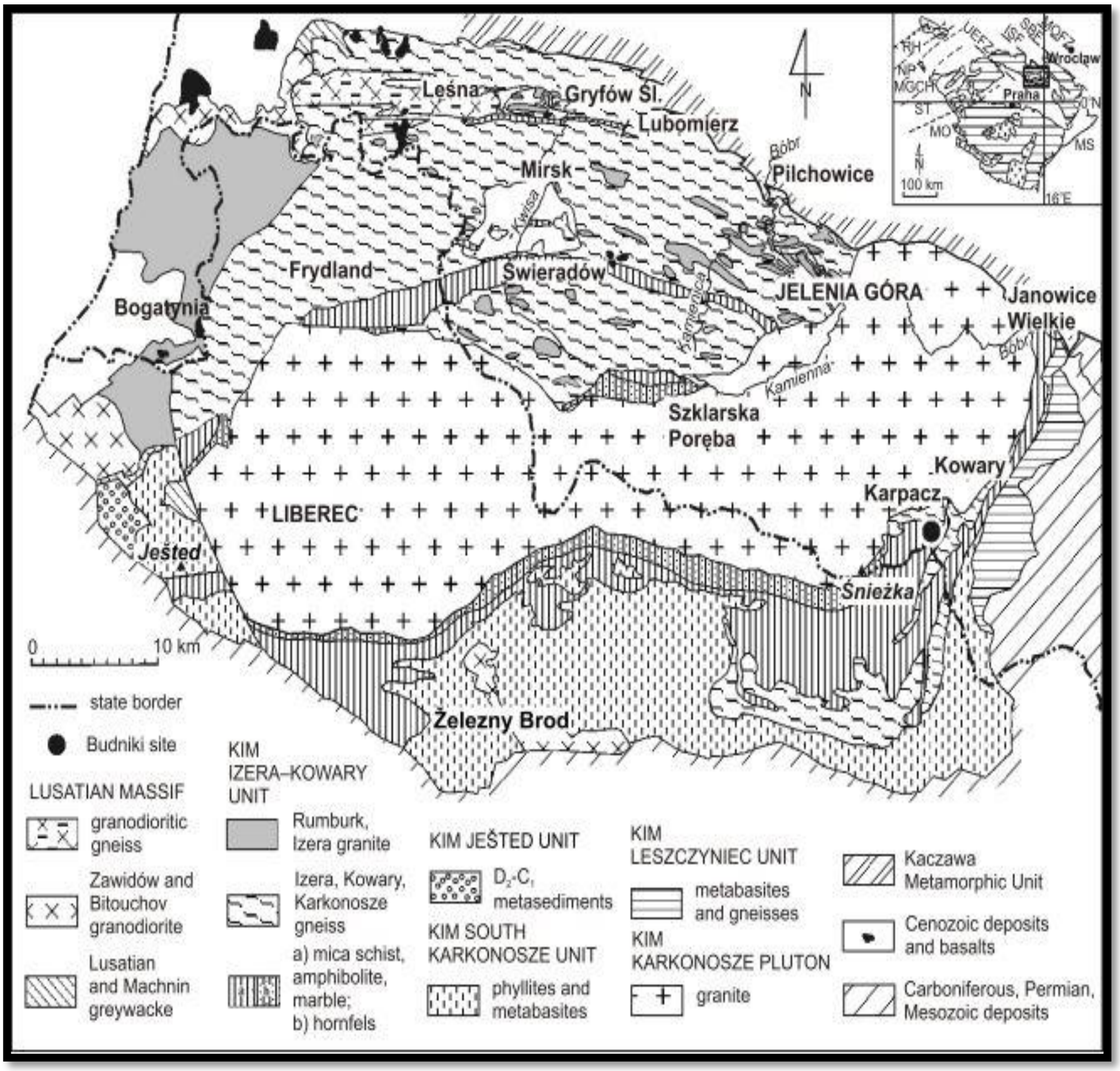


Fig 4. Geological map of the Karkonosze–Izera Massif (compiled from Chaloupský, 1989; Mazur, 1995; Mazur and Aleksandrowski, 2001; Oberc-Dziedzic, 2003)

3.4.1 Origin of the ore

The origins of mineralization are still a topic of debate. Cassiterite was thought to have originated as (1) sedimentary, syngenetic, and later metamorphosed (Szałamacha and Szałamacha, 1974); (2) hydrothermal, related to the granitic protolith of the Izera Gneiss (premetamorphic) (Cook and Dudek, 1994; Michniewicz et al. 2006); (3) hydrothermal, related to the Variscan evolution of the Karkonosze Granite Sulfides and sulfosalts are hydrothermal in origin; however, whether the source of hydrothermal solutions occurred in the Izera Granite or the Karkonosze Granite is a point of contention. The key reason for cassiterite's sedimentary origin is that there appears to be a link between cassiterite and the lithology of schist protoliths, as tin is mainly found in schists with garnets (Szałamacha and Szałamacha, 1974). However, it has been established that the geometry of ore zones does not necessarily match the shape of garnet-bearing zones (Michniewicz et al. 2006). The presence of cassiterite in paragenesis with sulfides and sulfosalts (Mochnacka 1985; Wiszniewska, 1984), as well as by sulfur isotope analyses (δ34S) in sulfides accompanying tin mineralization (Berendsen et al. 1987). However, it is still unclear whether the mineralization was emplaced before or after the Variscan orogeny.

Mineralization was the result of a long, telescoping process, with each phase of the process having a different spatial extent (Wiszniewska, 1984). Because there are some notable discrepancies in their spatial distribution, there was most likely a time gap between the emplacement of cassiterite and sulfides (Michniewicz et al. 2006).

3.4.2 Ore mineralization

The ore zones are commonly silicified and chloritized. Two tin minerals, stannite and cassiterite were found in the ore zones and the latter one is principal tin mineral in the area. Generally, cassiterite coexists with strongly ferrugineous minerals, including chlorite, garnet and quartz with iron content. Studies for structure and texture of ore paragenesis including fluid inclusions bring to distinguishing two stages of mineralization (Wiszniewska, 1984):

1. High temperature ranging from 250^{0}C to 550^{0}C where cassiterite play the main role in this stage.
2. Low temperature ranging between 100^{0}C and 250^{0}C that influenced stannite for low-temperature sulfide paragenesis.

Further, the ore minerals formed during both of the processes are added additionally into five different mineral association group according to their temperature range.

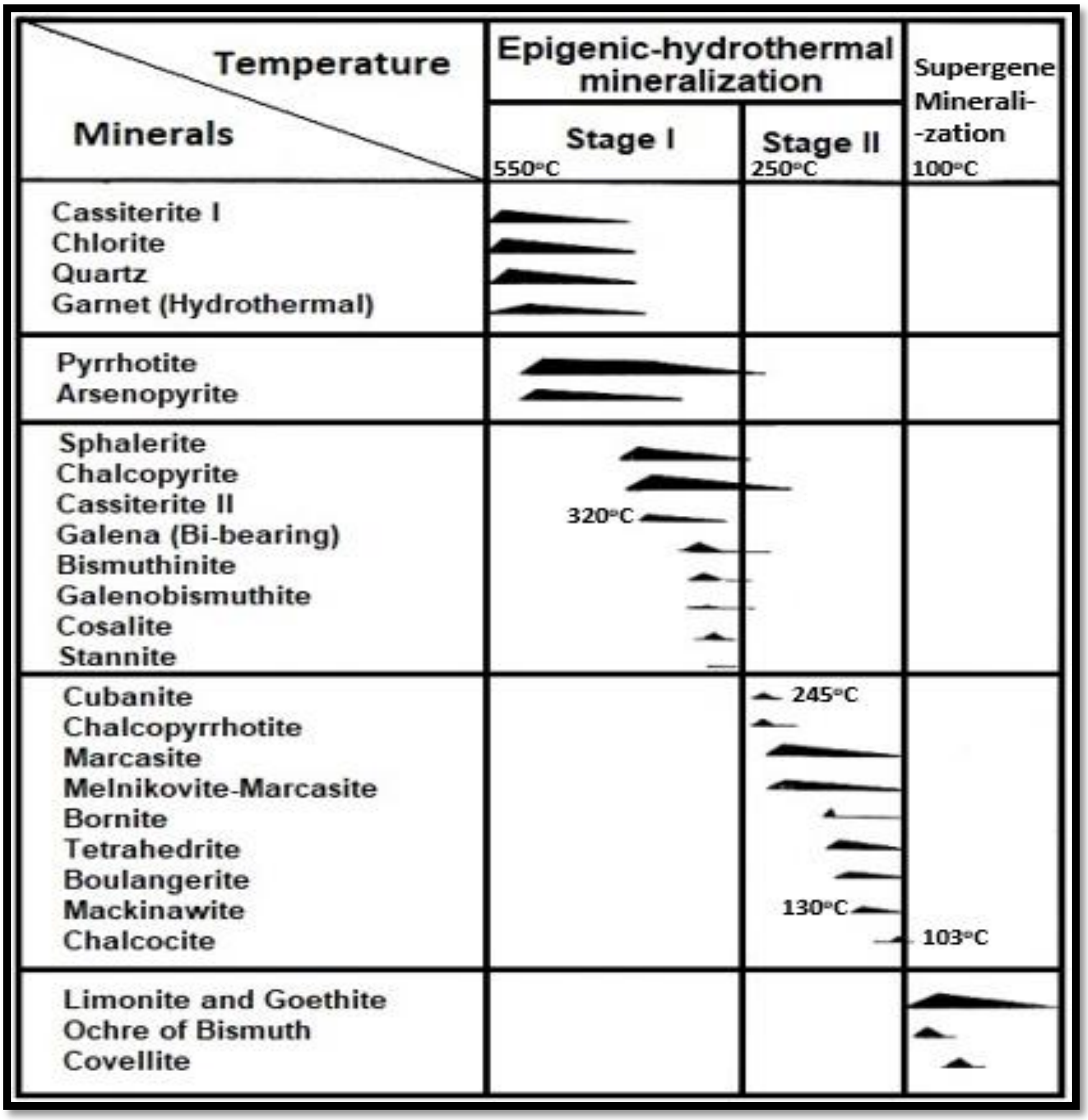


Fig 5. Ore mineral succession table in Stara Kamienica schist belt (Wiszniewska, 1998)

Generally, the groups are divided by two main groups, epigenetic-hydrothermal mineralization which ranging from 250^0C to 550^0C for first stage and 100^0C to 250^0C for the second stage and supergenetic mineralization which ranging up to 100^0C. According to the table, the group first until third group were formed in the first stage of epigenetic-hydrothermal process while the fourth group was deposited in the second stage. Lastly, the fifth group was formed in the supergenetic mineralization which ranging up to 100^0C.

3.5 Previous works

According to the literature study, there was a lot of studies and researches conducted in the area which observe the tin deposit from various aspects. There were three different opinions about the origin of the tin mineralization:

1. Novak (1960), Jaskolski (1963), Szalamacha (1975, 1976), Szalamacha and Szalamacha (1968) argue that the origin is Syngenetic-sedimentary process.
2. Petrascheck (1933), Jaskolski and Mochnacka (1959), Kozlowski and Karwowski (1975), Kozlowski (1978), Kowalski et al. (1978), Karwowski and Wlodyka (1981) assumed that it was an Epigenetic-hydrothermal process.
3. Stratiform exhalative-volcanogenic is proposed by Lehmann and Schneider (1981).

Further, Piestrzyński et al (1990) found the tin-tungsten mineralization system at Mirsk area in the norther part of the stara kamienica chain while Mayer et al (1996) published a preliminary report of rare earth element in the stara kamienica schist belt. Lastly, Pietrzela A (2019) reassess the Sn-Co mineralization in that area while Mikulski (2020) observe the occurrence of Indium-bearing in Stara Kamienica Schist belt.

CHAPTER III

METHODOLOGY

4 Materials and methods

To conduct the research, there are two different works conducted elaboratively to find the reliable result. Both the works are field work and laboratory work held respectively. Field work was conducted to collect the sample while the laboratory work is to observe and analyze the sample collected during the field work. All of the observation works are conducted in AGH University of Science and Technology at laboratory of Geology, Geophysics and Environmental Protection Faculty, except the chemical analysis conducted at Bureau Veritas Mineral Laboratories in Vancouver, Canada.

4.1 Field work

During the field work stage, the sample were collected in an open pit mine i.e a quarry where the mica schist is being mined. The quarry is situated in the Krobica area, a village under the Gmina Mirsk administrative district in Lower Silesian Voivodeship. Sample collected in the quarry are focused on the mica and garnet occurrence where both of the mineral is predicted contain higher amount of tin. After the sample collection in the area, all of the sample then moved to the laboratory for the laboratory work.

Fig 6. Sample collection during Field work in Schist Quarry, 2020

4.2 Laboratory work

This work is conducted to observe and analyze all of the sample collected from mica schist quarry in Krobica area where this work is divided by 5 steps including separation, preparation and some different analysis methods.

4.2.1 Separation

This stage is done to prepare samples for chemical analysis to be conducted at the Bureau of Veritas Mineral Laboratories in Vancouver Canada. The purpose of this analysis is to determine the chemical composition of the sample. In this stage, samples that have been collected from two different open pit mines in the Krobica area will be collected to separate garnet and schist. Samples that were previously in the boulder form will be selected and taken specific parts that are considered representative which will then be separated in the laboratory.

Fig 7. Garnet and schist separation under binocular

Selected parts with a sufficient and varied mineral composition will be separated using binocular and tweezers. For chemical analysis, 57.7 grams of garnet and 48.4 grams of schist were collected then put in a plastic bag before being sent to Vancouver, Canada for the chemical analysis.

Sample collected from two different locations are divided by 5 samples with different descriptions below:

Sample Name	Description
KRO-KAM-II-11	Basalt Dike
KAM-KRO-2	Chlorite schist with garnet vein
KAM-KRO-II-CHEM2	Mica schist with garnets and quartz
KAM-KRO-CH-1	Strongly deformed sericite schist
KAM-KRO-II-CHEM1	Mica schist
KAM-KRO-GRA-01	Red garnets from the quarry
KAM-KRO-GRA-02	Black garnets from the quarry

Table 1. Sample description for chemical analysis

The result of this analysis is the amount of mineral content contained in the sample which is calculated in ppm, ppb and percent units. In this stage there is a megascopic difference in garnet from the area where the garner from the first location is quite fresh while garnet derived from the second sample has undergone an alteration process so that it is slightly weathered than garnet from the first location.

4.2.2 Preparation

To find out the type and character of rocks from both areas, petrography analysis is needed. In petrography and mineragraphic analysis, rock examples need to be made a suitable preparation for the analysis to be carried out close to perfect. The result of this preparation consists of a thin section and polished section of a rock example. Thin section preparations are used for petrography analysis and polished sections for mineragraphic analysis. Optical characterization is performed using a polarizing microscope with transmitted and reflected light observation modes for petrography analysis (thin section analysis) and mineragraphic (polished section analysis) of rocks, particularly for ore characterization, but can also make observations of microscopic images on samples of other materials. The thin section is an example of a rock flattened and thinned on both sides to reach a thickness of about 0.03 mm and glued to the preparing glass, while a polished section is an example of a rock flattened one or more surfaces, then made molded using "Transoptic Powder". The purpose of making thin sections is the acquisition of preparations for petrography analysis, while the manufacture of polished sections to obtain sections for mineragraphic analysis.

Fig 8. Polished section sample of black garnet from quarry

The polarizing microscope in this laboratory is also equipped with cameras and data processing software that makes it possible to perform some simple analysis, such as microphotographic retrieval, distribution of grain size on the section, and so on. The number of samples predicted for microscopic observation is 7 samples with different characteristics in each sample.

4.2.3 Microscopic Observation

All of the samples were analyzed in AGH University of Science and Technology at laboratory of Geology, Geophysics and Environmental Protection Faculty using NIKON ECLIPSE E600 polarizing microscope in reflected and transmitted light. The observation was conducted to obtain the data about the petrology and mineralogy of the sample from both of polished and thin section.

4.2.4 Bulk chemical analysis

Chemical analysis is a determination of the physical properties or chemical composition of samples of matter using different detection limit. A large body of systematic procedures intended for these purposes has been continuously evolving in close association with the development of other branches of the physical sciences since their beginnings. Chemical analysis, which relies on the use of measurements, is divided into two categories depending on the manner in which the assays are performed. The analysis also termed wet chemical analysis, consists of those analytical techniques that use no mechanical or electronic instruments other than a balance, while every elements in the sample are analyzed and identified with different detection limit according to the table below:

LA-ICP-MS Detection limit in ppm					
Ag (0.1)	Ce (0.02)	Eu (0.01)	Lu (0.01)	Pr (0.01)	Sn (0.2)
Tl (0.2)	Zn (5)	As (0.2)	Co (0.1)	Ga (0.1)	Mn (1)
Rb (0.05)	Sr (0.1)	Tm (0.01)	Zr (0.5)	Ba (0.5)	Cr (1)
Gd (0.01)	Mo (0.2)	Re (0.01)	Ta (0.01)	U (0.01)	Be (0.2)
Cs (0.01)	Hf (0.01)	Nb (0.01)	Sb (0.1)	Tb (0.01)	V (0.1)
Bi (0.02)	Cu (2)	Ho (0.01)	Nd (0.01)	Sc (0.1)	Te (0.2)
W (0.05)	Br (10)	Dy (0.01)	In (0.05)	Ni (2)	Se (5*)
Th (0.01)	Y (0.02)	Cd (0.1)	Er (0.01)	La (0.01)	Pb (1)
Sm (0.01)	Ti (1)	Yb (0.01)			

Table 2. Detection limit for each element in ppm (Bureau Veritas Commodities Canada LTD, 2021)

The method usually relies on chemical reactions between the material being analyzed and a reagent that is added to the analyte. Wet techniques often depend on the formation of a product of the chemical reaction that is easily detected and measured. The analysis was conducted at Bureau Veritas Mineral Laboratories in Vancouver, Canada.

4.2.5 Wavelength-dispersive spectroscopy

MES offers WDS analysis for quick, quantitative chemical analysis of tiny particles. WDS (Wavelength Dispersive Spectroscopy Analysis) is a quantitative x-ray technique for determining the elemental makeup of materials fast and easily. Particle alloy detection, food product contaminant identification, and metal inclusion analysis are some of the applications. At borders, WDS can be utilized to determine homogeneity and elemental gradients. For airlines and other industries that require quick findings, MES delivers rapid alloy detection. WDS is a surface analysis technique that produces photoelectrons on the surface of a prepared sample using an x-ray beam. WDS systems are Scanning Electron Microscope (SEM) attachments that use the microscope's image capability to identify the specimen of interest. The beam generally penetrates the sample's outer 50 Angstroms. Diffracting crystals are used to isolate and interpret the photoelectrons. Prior to assessing an unknown composition, quantitative chemical analysis utilizing WDS is accomplished by collecting on NIST traceable standards. The research was carried out at the AGH University of Science and Technology's Geology, Geophysics, and Environmental Protection Faculty's laboratory.

CHAPTER IV

RESULT

4.1 Microscopic examination

4.1.1 Deformation

There was a deformation process in the area identified under the microscope where it was a post-kinematic garnet. In post-kinematic deformation, the garnet is formed after the deformation has taken place. The foliation has formed and then the garnets have grown across it causing no disturbs. There is no flowage of the foliation around the garnet. The original foliation in the areas of the rock where the garnets have grown over can be traced within the garnets as lines of inclusions - which are small particles of other minerals incorporated within the garnet as they grew in the solid state.

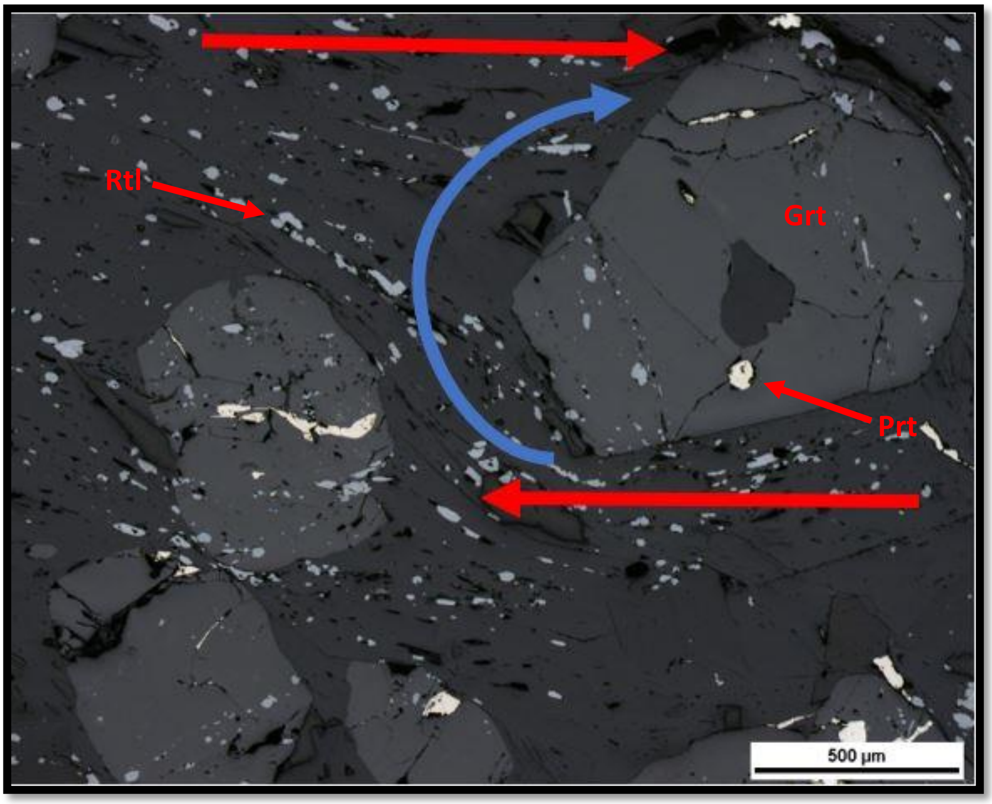


Fig 10. Post-kinematic Garnet (GRT) intruded by rutile (RTL) and Pyrite (PRT), reflected light, KAM-KRO 6.

According to the picture above, the red arrows show the shear stress direction that resulted the motion while the blue arrow determine the rotation of the garnet during the deformation. Because the process, some cracks were formed almost parallel to the foliation which influence some minerals like rutile and pyrite filled the cracks.

Similar with the garnet, the post-kinematic process textures also found in the other sample under the microscope that shows the sigmoidal structures trails of rutile inclusions in titanite formed during the metamorphic recrystallization.

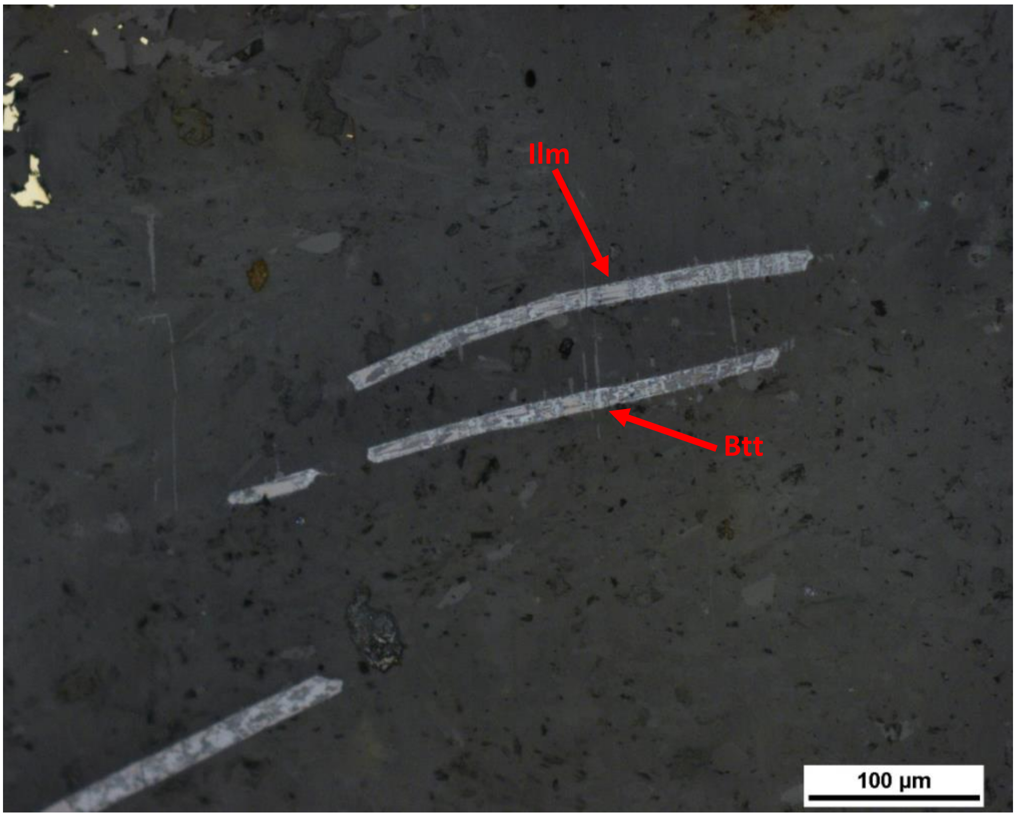


Fig 11. Post-kinematic deformation Biotite (Btt) with Ilmenite (Ilm), reflected light, KAM-KRO 11.

4.1.2 Ti mineralization

Ti-minerals are represented by ilmenite, rutile and titanite where the relationships between these minerals, their sequence and their position in the rock domains highlight the development of Ti mineralization and help to define more precisely the metamorphic conditions. Generally, there are two trends of Ti mineralization found during the observation. In the first variety of Ti mineralization is the Ti minerals are represented by clusters or aggregates of rutile, ilmenite and titanite which parallel the foliation; in places these are accompanied by minute grains of pyrite. The mutual inclusions: ilmenite in titanite and titanite in ilmenite are probably an effect of the section or indicate some retrogression. The structural position of ilmenite and titanite suggests that their crystallization was coeval with the deformation which produced the foliation.

In the second variety, the relationship between the minerals are more complicated where generally ilmenite formed earlier was replaced by titanite. This process usually begins at the margins of ilmenite crystals and gradually proceeds into the interiors, leaving small patches of ilmenite inside the titanite. The titanite rims around ilmenite, intergrown with rutile indicate that the replacement of ilmenite by titanite took place after the deformation and it affected only grains in the matrix which were not protected by the host plagioclase Occasionally, ilmenite is replaced by rutile.

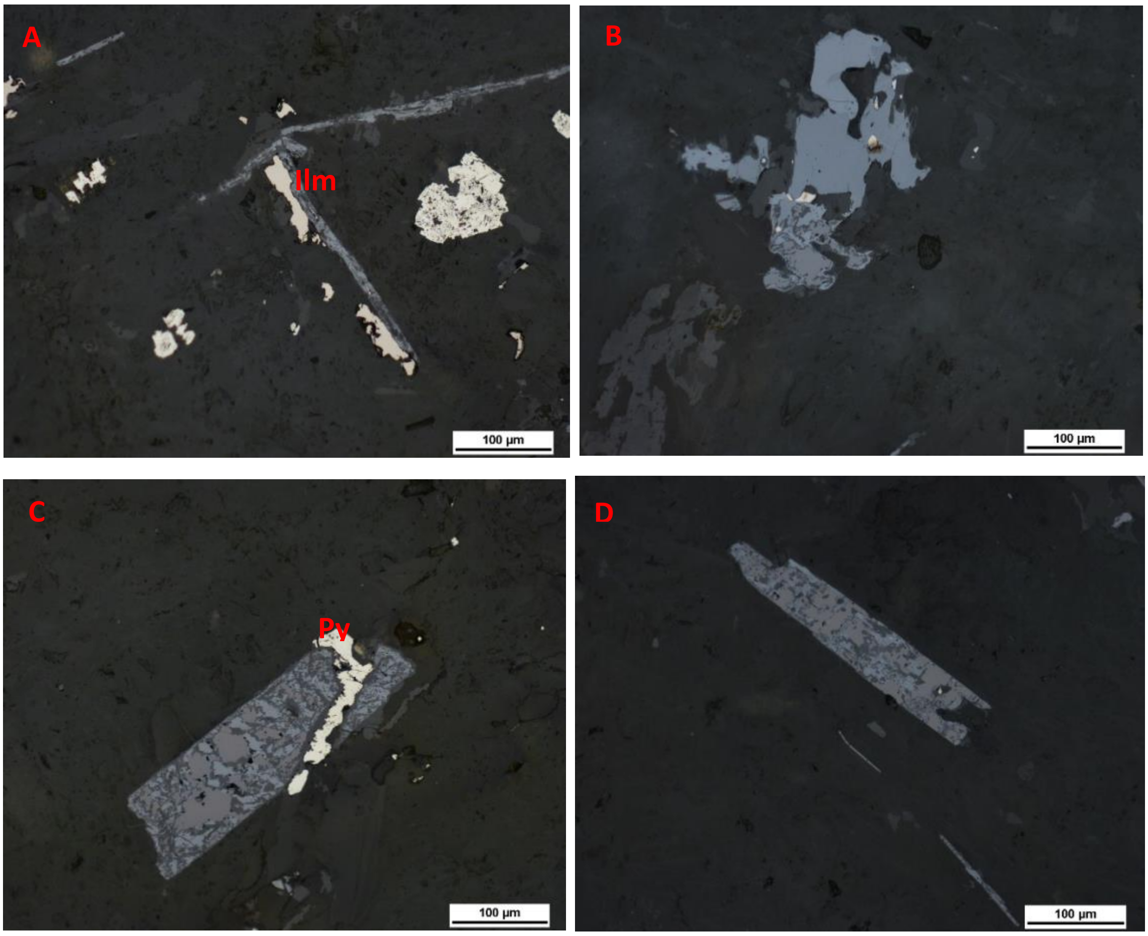


Fig 12. Images of Ti mineralization in reflected light

A-Pseudomorph after ilmenite composed of rutile needles forming a trigonal network; minute patches of titanite occur in the external part of the pseudomorph. **B**-Ilmenite grain patchily replaced by rutile rimmed by titanite and intergrown by pyrrhotite. **C**-Ilmenite patchily replaced by titanite intruded by pyrite. **D**- ilmenite patchily replaced by titanite

The replacement leads to the formation of rutile patches rimmed by titanite. Small inclusions of pyrite and pyrrhotite suggest that such replacement might have been caused by hydrothermal processes and might have used Fe released from ilmenite (Ramdohr, 1969). Another pattern of replacement leads to the appearance of rutile pseudomorphs after ilmenite composed of rutile needles forming a trigonal network. The pseudomorphs are associated with long, asymmetrically folded crystals of ilmenite. The rotation of pseudomorphs took place after the replacement and was coeval with the deformation of the amphibole nodule. The processes of mutual replacement of Ti minerals probably started at the end of the regional metamorphic event and became very intense during the contact metamorphism. The replacement processes were controlled by temperature, fluids, local mineral assemblages (chemical composition) and rock structures. The replacement of ilmenite by titanite was connected with retrogression at the end of the regional metamorphic event and/or at the beginning of the contact metamorphism, as well as during the late phase of the latter. The retrogression was enhanced by the presence of fluids and it caused the decomposition of plagioclases and the release of Ca and Al, facilitating the formation of titanite enriched in Al. Harlov *et al.* (2006) showed that the formation of Al-bearing titanite during amphibolite and greenschists facies metamorphism depends not only on P, T, bulk-rock composition and composition of the coexisting fluids but also on *f*O2 and *f*H2O.

4.1.3 Sulphide mineralization

Microscopy observations revealed the presence of a diversified assemblage of ore minerals. Besides Ti phases and enclosed, the ore assemblage is also composed mainly of pyrrhotite, pyrite, chalcopyrite, and sphalerite. The ore minerals form disseminated, spotty, streaky and veinlet structures within various types of amphibolites. Because the samples were collected exclusively from operated schist quarry where the oxidation process is running very quick, it is impossible to evaluate the relationships between the various ore structures.

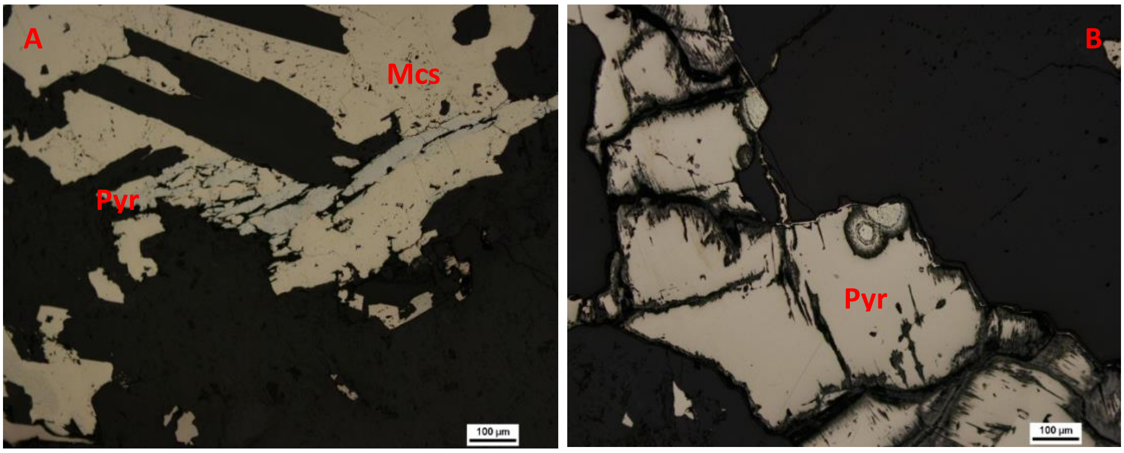


Fig 13. Sulphide mineral occurrence in reflected light; **A-**Replacement of pyrrhotite (Pyr) by marcasite (Mcs). **B-**Oxidation process of pyrrhotite (Pyr)

Pyrrhotite forms disseminated and spotted structures. Some grains are arranged concordantly with the foliation, while other, larger, isometric or elongated aggregates are commonly intergrown with gangue minerals. Pyrrhotite forms intergrowths with chalcopyrite. Both phases seem to be contemporaneous. Pyrrhotite crystals are commonly replaced by marcasite which rims its grains and grows inside, along cleavage planes.

Moreover, the oxidation process in the area is very clear under the microscope indicated by the presence of some bird eye texture of the pyrrhotite.

4.2 Bulk chemical analysis

Based on the results of chemical analysis conducted by ACME at the Bureau of Veritas Mineral Laboratories in Vancouver Canada, data obtained in the form of the amount of content of several elements contained in the sample. In visualizing the data, there are four groups based on units of its composition in ppm, ppb, percent and rare earth element in ppm units which will be explained in several parts.

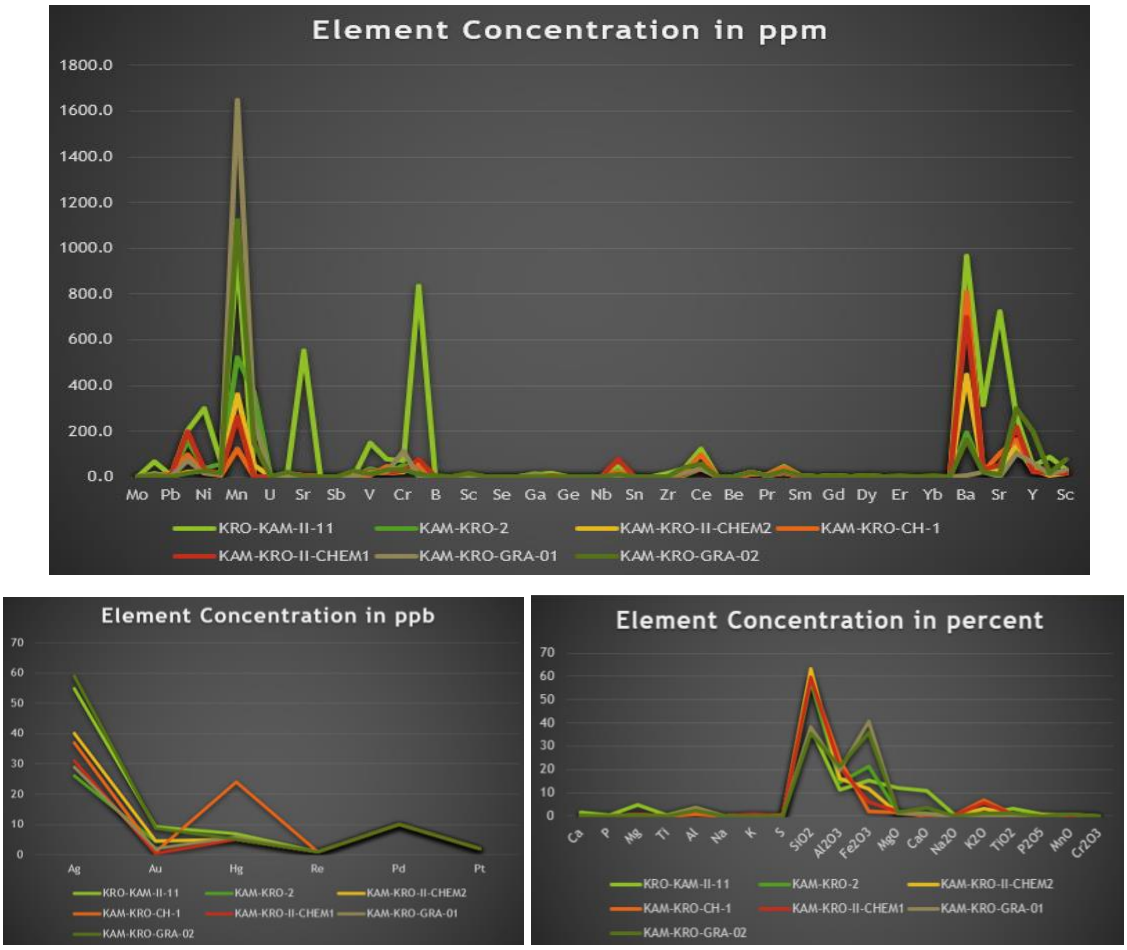


Fig 14. Element concentration in several units from chemical analysis

According to the chemical composition result, there are several elements which very low contain then below the detection limit of the equipment while some elements show a very interesting amount. The graphs above provided that the concentration of Mn, Sr, B, Sn, Ce, Ba, Sr, Y, Ag, Mg and Pd show their own peak. Special for rare earth element member, some elements member reveals an anomaly according to their higher amount. Generally, all of the REE member were detected above the detection limit but interestingly, some of them are higher than element average content of their occurrence. Further, La, Ce, Nd, Gd, Dy, Er, Yb and Sc show the higher amount but the most interesting result is the content from KRO-KAM-II-11, KAM -KRO-CH-1 and KAM-KRO-GRA-02 are mostly higher than the others. the significant differences in the contents of the elements may influenced by their metamorphic and/or post-metamorphic event in the past.

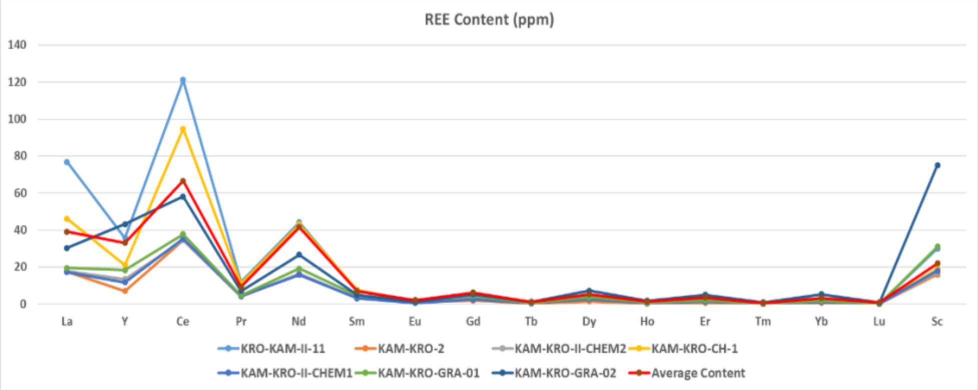


Fig 15. Rare earth element concentration

4.3 Wavelength-dispersive Spectroscopy (WDS)

During the Wavelength-dispersive Spectroscopy (WDS) observation, there are two interesting minerals which are analyzed in the laboratory. The observation was conducted to determine the composition and mineral group of the garnet and tourmaline. The result of this observation will lead the determination of the deposit type of the tin in the research area.

4.3.1 Garnet

There were 114 observation points spotted in the sample to obtain the chemical composition of the garnet. Some elements such as Ca, Ti, Mn, K and Zn are very low amount then below the detection limit. It will influence the calculation result where only Na, Mg, Al, Si and Fe which will be calculated to determine the minerals occurred in the garnet. During the calculation, author was accompanying with webmineral.com, a website which provide some formulas to calculate and distinguish the mineral composition. The result of the calculation reveal that Si, Mg and Al are very dominant in the garnet while the others are relatively low. It will influence the grouping of the mineral member where the Garnet mineral group is divided by two groups; Aluminum members and Calcium members.

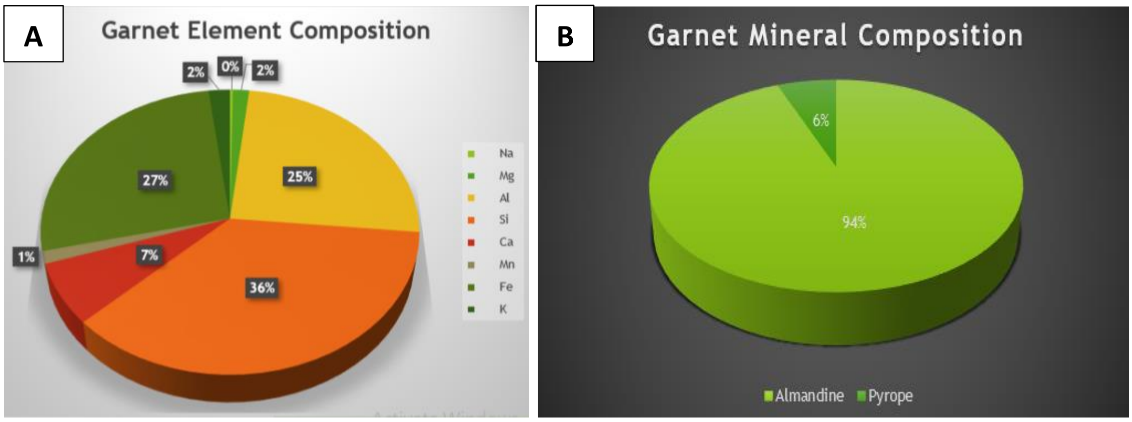


Fig 16. WDS result of Garnet; **A**-Garnet element composition. **B**-Garnet mineral group

Based on the result, the higher amount of aluminum in the garnet led to the mineral group occurs in the garnet. As a result, almandine is very dominant around 94% from whole observation point while pyrope only accounted 6%. Occurrence of both of the garnet mineral is influenced by the higher amount of aluminum deposited in the sample.

4.3.2 Tourmaline

Less than the garnet, observation point in tourmaline only 65 points and detect a lot of elements but some of them are below the detection limit. Only Al, Si, Fe, Ti, Cs and Na detected above the detection limit. All of these elements also will be calculated under the guiding of webmineral.com. Similar to garnet, Si and Al are very dominant followed by Fe.

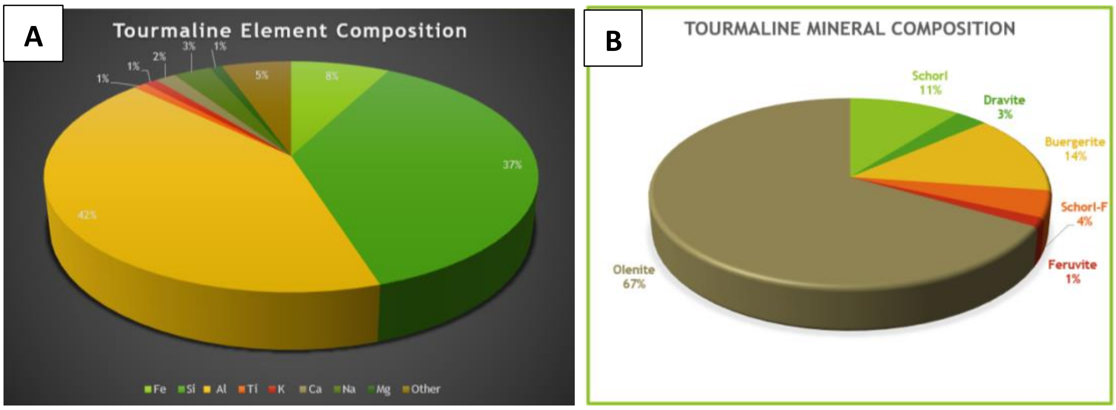
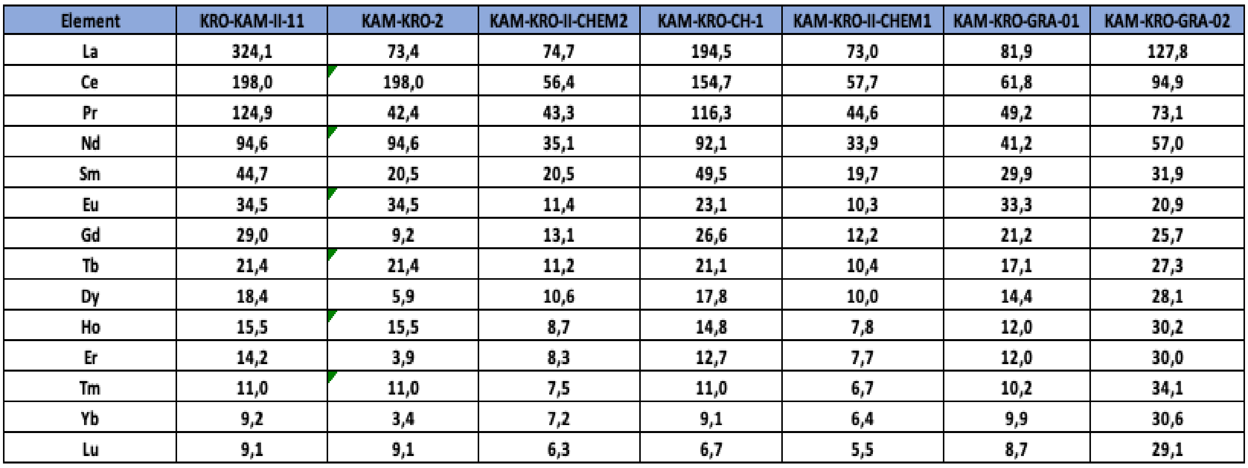


Fig 17. WDS result of Tourmaline; **A**-Tourmaline element composition. **B**-Tourmaline mineral group

According to the result, the higher amount of Si and Al led to the grouping of the mineral occurred in tourmaline. Most of them are Olenite about 67% while Schrol-F and Schrol around 14% and 11% respectively. The occurrence of tourmaline in the sample also will influence the analyze for of deposit type in research area.

4.3.3 Rare earth element

The lanthanide elements are categorized as light-group rare earth element (LREE) and a heavy-group rare earth element (HREE). The lepton configuration of each rare-earth element is used to define associate LREE and HREE. The LREE are lanthanum (atomic number 57) through gadolinium (atomic number 64). The LREE all have increasing numbers of unmated electrons, from zero to seven. Terbium, atomic number 65, through lutetium, atomic number 71, make up the HREE. All of the HREE are affected by the primary eight lanthanides' requirement for 'paired' electrons (a right-handed associated counter-clockwise spinning election). There are no paired electrons in the LREE. Due to its identical ionic radius and chemical characteristics, a metallic element is enclosed within the HREE cluster. Although atomic number 21 is also trivalent, its other qualities aren't similar enough to identify it as an LREE or HREE.



Element	KRO-KAM-II-11	KAM-KRO-2	KAM-KRO-II-CHEM2	KAM-KRO-CH-1	KAM-KRO-II-CHEM1	KAM-KRO-GRA-01	KAM-KRO-GRA-02
La	324,1	73,4	74,7	194,5	73,0	81,9	127,8
Ce	198,0	198,0	56,4	154,7	57,7	61,8	94,9
Pr	124,9	42,4	43,3	116,3	44,6	49,2	73,1
Nd	94,6	94,6	35,1	92,1	33,9	41,2	57,0
Sm	44,7	20,5	20,5	49,5	19,7	29,9	31,9
Eu	34,5	34,5	11,4	23,1	10,3	33,3	20,9
Gd	29,0	9,2	13,1	26,6	12,2	21,2	25,7
Tb	21,4	21,4	11,2	21,1	10,4	17,1	27,3
Dy	18,4	5,9	10,6	17,8	10,0	14,4	28,1
Ho	15,5	15,5	8,7	14,8	7,8	12,0	30,2
Er	14,2	3,9	8,3	12,7	7,7	12,0	30,0
Tm	11,0	11,0	7,5	11,0	6,7	10,2	34,1
Yb	9,2	3,4	7,2	9,1	6,4	9,9	30,6
Lu	9,1	9,1	6,3	6,7	5,5	8,7	29,1

Table 3. REE normalization value after McDonough & Sun (1989)

After the normalization using chondrite normalization factor by McDonough & Sun (1989), the LREE is more abundance than HREE in both of the garnet and mica schist samples. The La shows the highest amount than the others element then followed by Ce, Pr, Nd, Sm, Eu and Gd respectively while the HREE members reveal almost similar concentration. Specifically, typical of the samples divided by garnet and mica schist provided a similar trend in value. But, KAM-KRO-GRA-01 described as red garnet and KAM-KRO-GRA-02 as black garnet from the quarry contain more REE than the other samples described as mica schist.

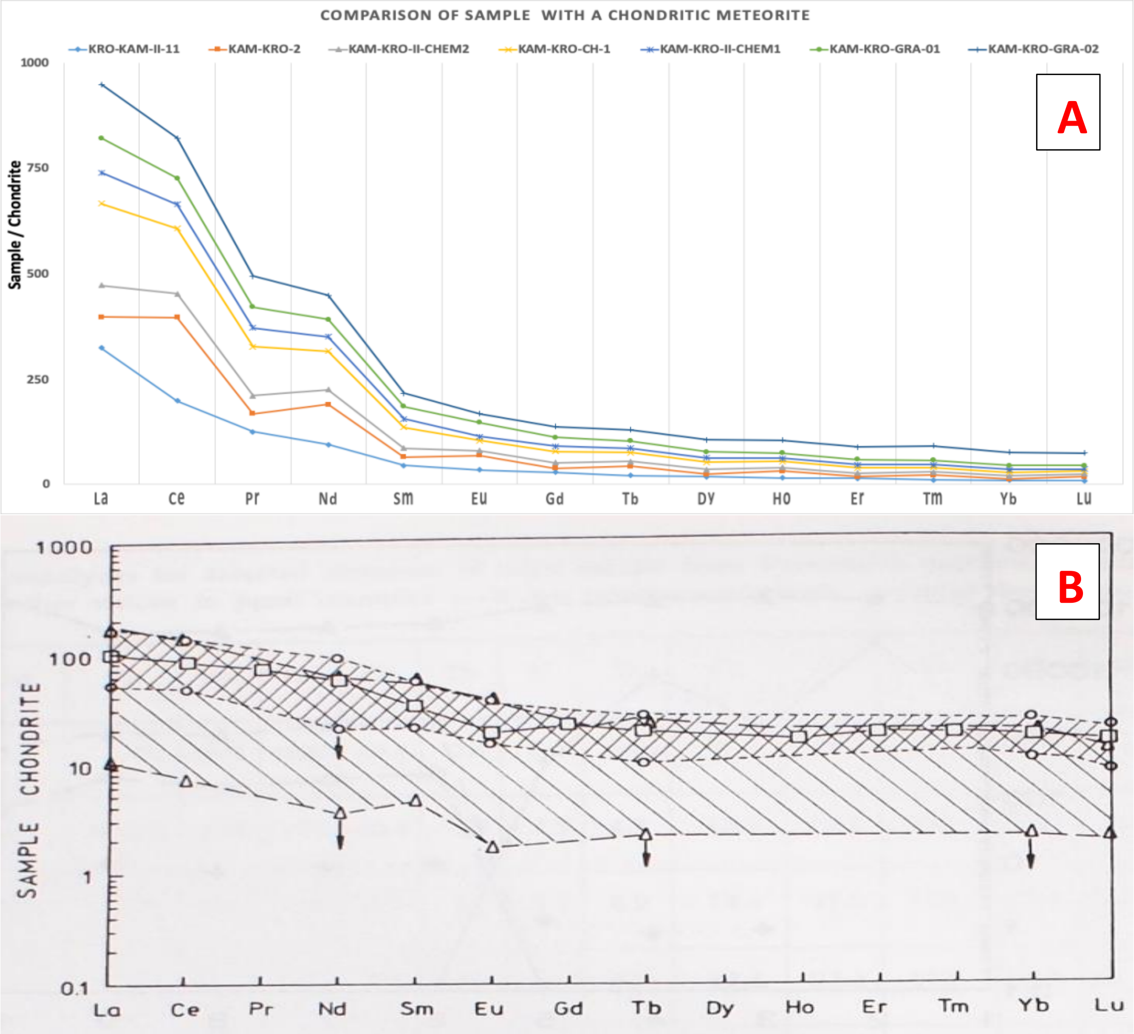


Fig 18. **A-**REE normalization graph after McDonough & Sun (1989), **B-**REE distribution pattern of Schist in Przecznica area at Sudety Mountain, Mayer W (1996) after Haskin et al (1968)

According to the comparison of the REE concentration from bulk chemical analysis and the pattern of REE in schist at sudety mountain from Mayer W (1996), there is a similarity trend concentration on whole element. The area is identified well as the greenschist metapelitic facies according to Grauch (1989). Influence of the karkonosze granite in mica schist of Stara Kamienica cahin play a main role in REE mineralization. The pattern indicates two different processes connected to the REE mineralization: regional metamorphism process influenced the schist sequence then metasomatosis which formed the tin-bearing zones.

CHAPTER V

DICUSSION

5.3 Deposit type

Occurrence of garnet and tourmaline have a strong relationship to the deposit type of the garnet in the research area. Based on several examinations, garnet and pyrrhotite indicated the Sn-Polymetalic sulphide deposit while tourmaline is connected to Sn-Greisenized (Sn-W) type. Some evidences from the analysis also identify occurrence of Zirconium which will provide an hypothesis about the mineralization system in research area.

5.3.1 Sn-Polymetalic Sulphide Type

Garnet was divided into two generations. Garnet of the first generation is often automorphic, with elongated ilmenite and rutile inclusions. The genesis of this garnet is thought to be metamorphic. The garnet associated with cassiterite I, quartz, and/or chlorite is xenomorphic, elongated in accordance with ore-bearing zones, and free of ilmenite and rutile inclusions. It does, however, contain cassiterite, chlorite, and quartz intergrowths. I believe this garnet, along with cassiterite and chlorite, came from a hydrothermal source. Intergrowths of arsenopyrite, pyrrhotite, and cobaltite in hydrothermal garnet have been observed in some preparations. This backs with Petrascheck's earlier findings (1933). Hydrothermal garnet was discovered in several cassiterite-quartz-chlorite ore layers in Sikhote Alin (USSR) and was also characterized from Mirsk's greisen rock (Karwowski 1977). Jaskolski (1963) and Szalamacha (1976) observed a positive correlation between the amount of garnet and cassiterite in schists, which was utilized as evidence for the syngenetic origin of these deposits. This form of association, on the other hand, was discovered in this study.

Similar to chemical analysis result, it shows an impressive amount of tin in some sample contained garnet. If GRA-01 and GRA-02 are red and black garnet collected from the quarry, KRO-2 and CHEM-2 are associated with chlorite schist and mica schist. Further, the examination of tin bearing-bearing paragenesis, especially the composition of garnet which show presence of chlorite and/or pyrrhotite inclusions in garnet may form evidence for thr post-metamorphic genesis for chlorite and garnet or their formation during late metamorphic process

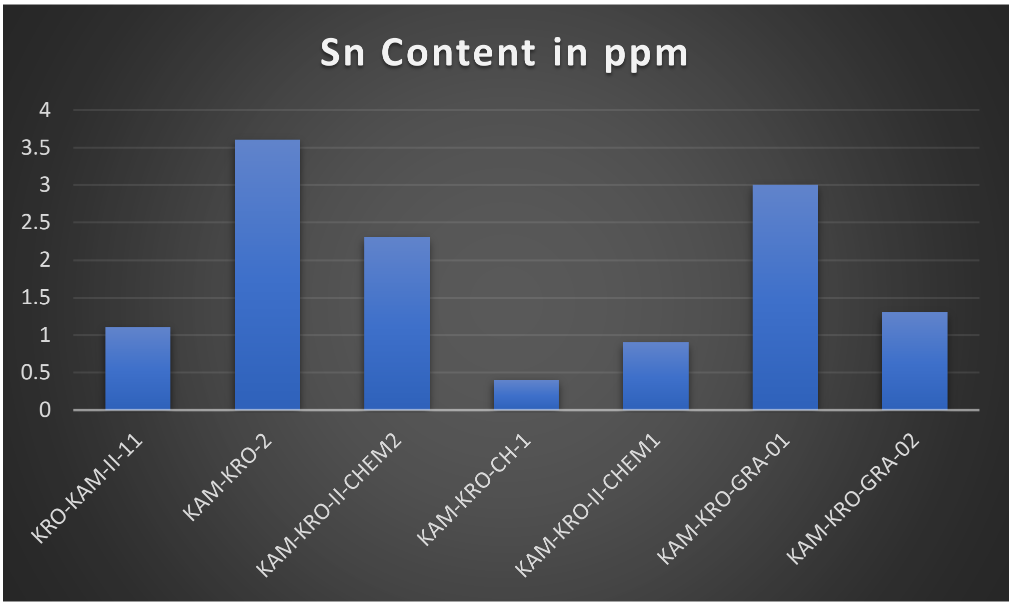


Fig 19. Sn concentration from chemical analysis result

5.3.2 Sn-Greisenized (Sn-W) Type

The discovery of tourmaline in samples identified under a microscope indicates the existence of a type Sn-Greisenized (Sn-W) deposit type in the research area. This is supported by the results of chemical analysis where the concentration of tungsten in KRO-2, CHEM-2, GRA-01 and GRA-02 are quite high where the samples are also contains garnet.

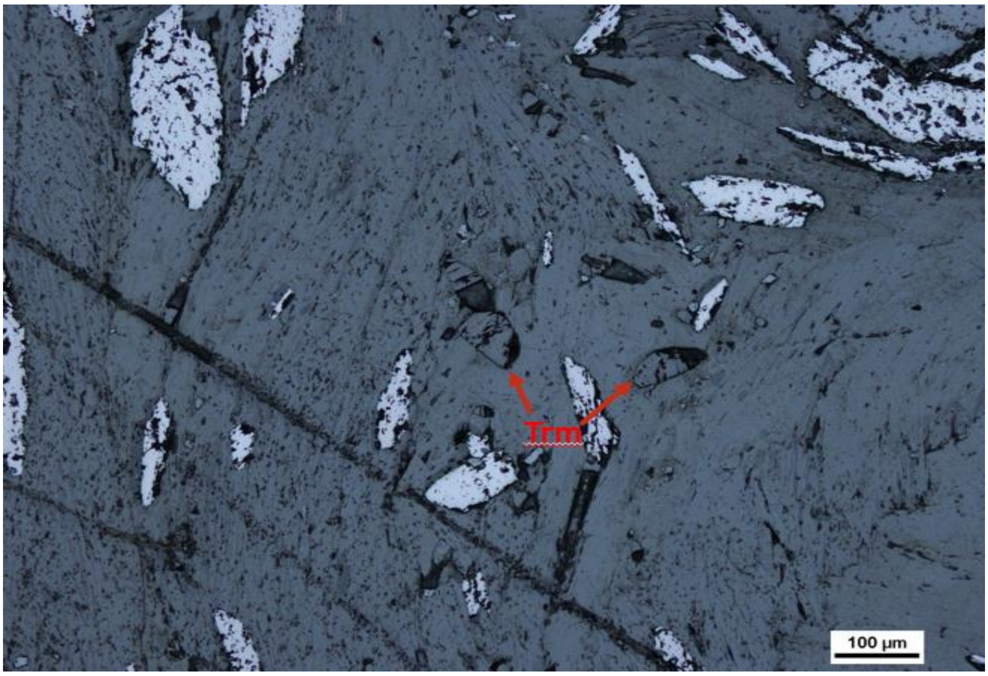


Fig 20. Tourmaline occurrence in rounded shape, reflected light, KAM-KRO II 13

Piestrzynski et al (1990) have identified the Tungsten mineralization in tin deposits using scheelite and ferberite as an indicator in the Mirsk area situated in the northern part of the research area. With the findings of tourmaline in the research area, it can be assumed that the process of deposition of tin in this area has a close relationship in according to their tourmaline occurrence.

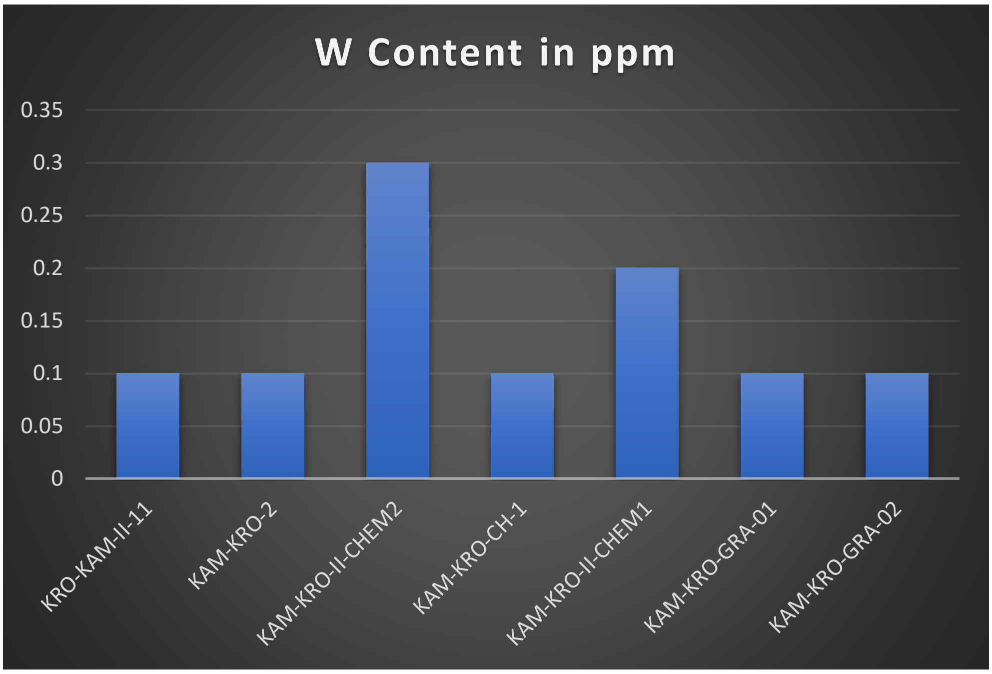


Fig 21. Tungsten content from chemical analysis result

5.4 Zr-Sn Mineralization system

In addition to tourmaline zirconium is also found in some samples using polarizing microscopes. At some point, tourmaline was found to be directly adjacent to ilmenite which is an indicator mineral of Ti remobilization.

The zirconium were founded in rounded or dotted shape which intergrowth with ilmenite that indicate the relation between the Ti remobilization and the different tin mineralization system among the mica. In some publications it is mentioned that the discovery of zirconium in tin deposits can be used as an indicator of the existence of Zr-Sn Mineralization system in the area

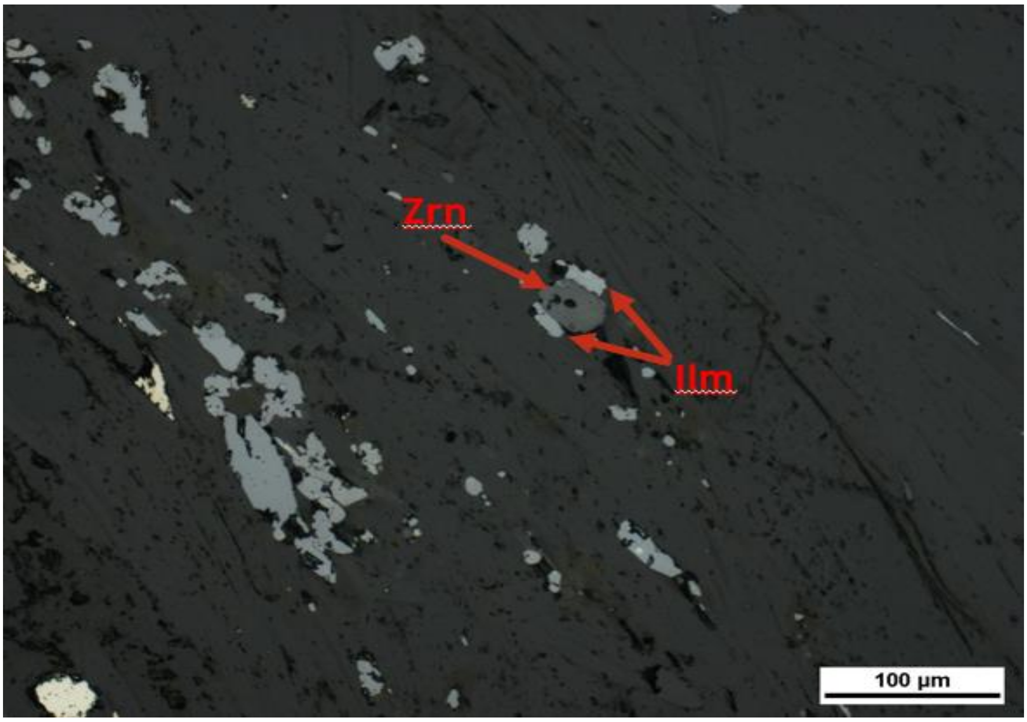


Fig 22. Zirconium intergrowth with ilmenite in mica, reflected light, KAM-KRO 18

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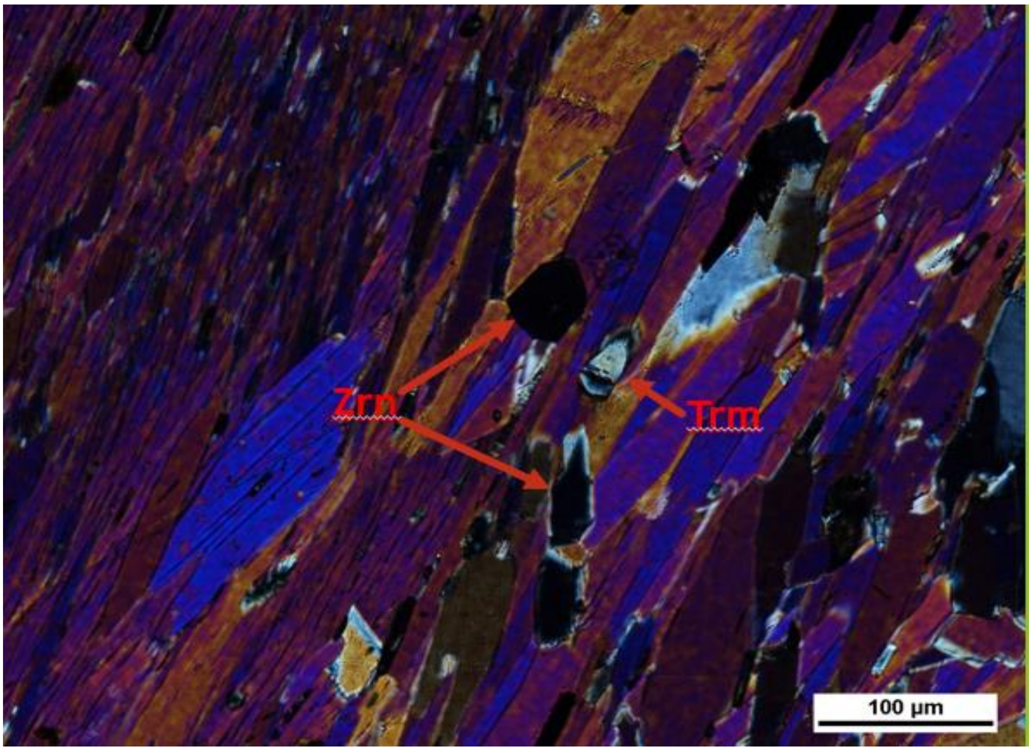

Fig 23. Zirconium and tourmaline occurrence in schist, transmitted light, KAM-KRO 18

According to the rounded and dotted shape, it indicated that zirconium was formed during or after the metamorphism process.

CHAPTER VI

CONCLUSION

Although the genesis of mineralization is still debated, I contend that the tin deposit in the study region is sedimentary, syngenetic, and later metamorphosed. It is induced by the sedimentary genesis of cassiterite and pyrrhotite, which is linked to the lithology of schist protoliths, because tin is found predominantly in schist enriched with garnet, but ilmenite and rutile are thought to have a sedimentary (allogenic) origin. Further, based on the result and analyze, I conclude that:

1. Garnet in the area is categorized as Aluminum member garnet while tourmaline is categorized as Al-rich tourmaline group.
2. According to the result of several examinations and discussions, there are two types of tin deposit in western part of stara kamienica schist chain; Sn-Polymetalic Sulphide Type and Sn-Greisenized (Sn-W) deposit type.
3. Presence of zirconium in several samples indicate the Zr-Sn mineralization system in western part of stara kamienica schist belt.

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