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Suitability of Finnish mine waste (rocks and tailings) for Mineral Carbonation

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Abstract:

Finland has no suitable sedimentary deposits for CO₂ storage which is why Carbon Capture and Mineralisation (CCM) is the most promising way for storage of anthropogenic CO₂. A mineral carbonation method has been developed at Åbo Akademi University. In the carbonation process Mg is extracted from the raw material, converted into Mg(OH)₂ and subsequently fused with CO₂ in an exothermic reaction forming stable magnesite, MgCO₃. This paper discusses the essential characteristics of mine waste products in Finland and their suitability for CCM, in order to get the maximal economical gain. Materials are provided by varying mines in Finland. Tailings have not been studied before for this purpose. The results suggest that mine waste consisting of ultramafic rocks that contain phyllosilicate with >17% Mg and >2.5% of crystallisation H₂O make for the most profitable material.

Keywords:

Mineral carbonation, Carbon capture and mineralisation (CCM), Mine waste, Mine tailing.

1. Introduction

The objective of this study is to develop a method to reduce human produced CO₂ -emissions to the atmosphere. Anthropogenic CO₂- emissions have been linked to global warming and one solution has been the capture and storage (CCS) of these emissions. The captured CO₂ can be stored for example in deep sea sediments or empty gas and oil fields. Finland lacks geological formations for carbon capture and storage. Therefore this study focuses on carbon capture and mineralization (CCM) as a possible sink for anthropogenic CO₂. Mineral carbonation with naturally occurring silicate minerals is considered to be the only possible storage option in countries like Finland where suitable geological formations do not exist [1]. The units of Thermal and Flow Engineering Laboratory and Geology and Mineralogy at Åbo Akademi University have developed methods and achieved good results on CCM [2]. In order to get the maximal gain in the process, the used raw material has to be properly characterized. The mineralogical characteristics were studied with a microscope, X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Scanning Electron Microscope (SEM). Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for analysing the Mg-extraction and -precipitation achieved with the carbonation method developed at the Thermal and Flow Engineering Laboratory. Production of magnesite from ultramafic rocks for CCM is expensive because of grinding and transporting costs of the raw material. Therefore it will be an advantage if the carbonating process will take place where suitable material is available on site. Using by-products from active mines would be a benefitting factor, especially if mine tailings show potential for carbonation processes. Mafic and ultramafic rocks with hydrous Mg-rich silicates have been stated to be the most promising raw material for mineral carbonation [2]. Study material was therefore collected from particular mines located on the ultramafic areas of Finland. There are large amounts of anthropogenic waste materials that would be usable for further exploitation. By developing the method for mineral carbonation it is possible to make good use of

both mine waste and CO₂-emissions, which together produce a green raw material for example within the construction industry. The results of this study can be applied for selecting suitable raw materials for mineral carbonation. Knowledge of the optimal geological and mineralogical parameters is essential, as rocks and minerals should be selected in order to achieve profitable raw material for CCM.

2. Material

This study focuses on ultramafic rocks (low in SiO₂ (<45%) and high in MgO (>18%) as they show the most potential for mineral carbonation [2]. Studied mine tailings are from the same mines as the rocks on focus which is why they should represent the rock types of the mines. Four of the investigated mines contain Mg-rich minerals in their host rocks: olivine (Mg,Fe)₂SiO₄, clinopyroxene Ca(Mg,Fe)Si₂O₆, serpentine (Mg, Fe)₃Si₂O₅(OH)₄, talc Mg₃Si₄O₁₀(OH)₂ and chlorite (Mg₅Al)(AlSi₃)O₁₀(OH)₈. Previous studies [2][3] have shown that serpentine, that contains crystallisation water, disperses faster in the reaction with ammonium sulphate ([NH₄]₂SO₄) compared to “dry” minerals like olivine and pyroxenes. Additional hydrous minerals, talc and chlorite, were introduced to this study. Since olivine and pyroxenes can be altered to serpentine through serpentinization, an olivine-pyroxenite rock was added to the study material.

2.1. Rock material

This study included samples from five mines in Finland: Hitura (HIT) (nickel-mine situated in a serpentinite), Kevitsa (KEV) (multi-metal ore mine situated in an ultramafic olivine-pyroxenite), Pampalo (PAM) (gold mine situated in rocks containing talc-chlorite schists), Mondo Minerals (POLVI) (the second biggest producer of talc with ores constituting almost solely of talc) and Talvivaara (TALVI) (processes Ni-rich black schists) (see Table 1). Four samples were excluded from further studies as they did not show any CCM-potential based on their mineralogy. Excluded rocks were quartzite, black schist, mica schist and a mafic volcanite. Rocks considered as potential raw material for CCM were serpentinites (samples HIT1, HIT2, HIT3 and POLVI1), an andesite-tuff (PAM1), an iron formation (PAM3), a chlorite-talc schist (PAM4) and an olivine-pyroxenite (KEV1).

Table 1. Mines and their rocks included in this study. Samples below the dashed line are rocks excluded from the study based on their mineralogy.

Samples	HITURA	KEVITSA	PAMPALO	MONDO MINERALS	TALVIVAARA
	HIT1, HIT2, HIT3	KEV1	PAM1, PAM3, PAM4 (PAM2)	POLVI1	(TALVIQ, TALVIKL, TALVIML)
Serpentinite	X			X	
Pyroxenite		X			
Chlorite-talc schist			X		
Andesite-tuff			X		
Iron formation			X		
Mafic volcanite			X		
Mica schist					X
Black schist					X
Quartz					X

Serpentinites from the Hitura mine present a gangue, a fresh barren ore, straight from the mine (HIT3), a similar sample that had been stored outside for two years (HIT1) and a sample that had been stored outside for 15 years (HIT2). All of them were processed in order to compare how weathering affects the results. Percentages for primary and secondary minerals in samples were quantified ocularly from bulk rocks and thin sections of the samples.

2.1.1 Serpentinite - Samples HIT1, HIT2, HIT3 and POLVI1

All samples are ultramafic rocks metamorphosed in greenschist facies. They present an evengrained rock with magnetite (Fe_3O_4) and pyrite (FeS_2) veins (\varnothing 0,5 - 2mm). 90 % of the samples consist of serpentinite, 5 % of magnetite and pyrite and 5 % of subhedral biotite ($\text{K}(\text{Mg},\text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{F},\text{OH})_2$) /opaques. Some naturally occurring carbonates are also present (Appendix B. Figs. a-d).

2.1.2 Andesite-tuff - Sample PAM1

The sample is an andesite-tuff with a porphyritic texture. Matrix consists of quartz SiO_2 , hornblende ($(\text{Ca},\text{Na})_{2-3}(\text{Mg},\text{Fe},\text{Al})_5(\text{Al},\text{Si})_8\text{O}_{22}(\text{OH},\text{F})_2$) and biotite while porphyries consist of plagioclase ($(\text{Na},\text{Ca})(\text{Si},\text{Al})_4\text{O}_8$), clino- ($(\text{Ca},\text{Mg},\text{Fe},\text{Na})(\text{Mg},\text{Fe},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$) and orthopyroxenes ($(\text{Mg},\text{Fe},\text{Ca})(\text{Mg},\text{Fe},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$). Despite its high plagioclase content (~40 %), the sample was included in the study because it contained ~40 % biotite that may contain up to 18 % wt.% Mg. (Appendix B. Fig. e)

2.1.3 Iron formation - Sample PAM3

The sample is a strongly migmatized iron formation with well-developed lineation. It is fine- to medium-grained with occasional talc veins. The overall appearance of the sample is “rusty”. Primary minerals are stilpnomelane ($\text{K}(\text{Fe}^{2+},\text{Mg},\text{Fe}^{3+})_8(\text{Si},\text{Al})_{12}(\text{O},\text{OH})_{27}\cdot n(\text{H}_2\text{O})$) and hornblende. This sample was included in the study because of its high iron content. (Appendix B. Fig. f)

2.1.4 Chlorite-talc schist - Sample PAM4

The sample is a chlorite-talc schist (chlorite $(\text{Mg},\text{Fe})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2\cdot(\text{Mg},\text{Fe})_3(\text{OH})_6$), talc ($\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ or $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) with light chlorite green color. Talc in the sample easily rubs off. ~50 % consist of talc, ~45 % of chlorite and ~5 % of pyrite, magnesite and opaques. (Appendix B. Fig. g)

2.1.5 Pyroxenite - Sample KEV1

The sample is a dark green fine-grained pyroxenite with occasional smaller grains (\varnothing 1 - 2mm). It consists mostly of pyroxenes and amphiboles (<80 %). Secondary minerals are biotite, plagioclase, iron oxides, magnetite and olivine ($\text{Fe},\text{Mg})_2\text{SiO}_4$). The sample was included in the study because it was originally stated as olivine-pyroxenite and olivine was wanted for the study. Later experiments showed that the sample did not contain any olivine. (Appendix B. Fig. h)

2.1.6 Mafic volcanite, quartzite, mica schist and black schist – Excluded samples PAM2, TALVIQ, TALVIKL and TALVIML

PAM2 is a foliated porphyritic fine-grained mafic volcanite. It was excluded from the study as its primary minerals are amphibole and plagioclase (~70 %). Secondary minerals are biotite, quartz, magnetite and opaques. The sample was excluded from further studies because its primary minerals either do not donate their Mg (amphiboles) [4] or do not contain any Mg (plagioclase). (Appendix B

Fig. i) TALVIQ is a quartzite with fine- to medium-sized evenly distributed grains. It consists of quartz (SiO_2) with biotite and muscovite ($\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$) as secondary minerals. This sample was excluded from further studies because its primary mineral does not contain any Mg. (Appendix B. Fig. j) TALVIKL is a fine-grained mica schist that consist mainly of quartz and plagioclase with biotite and ilmenite (FeTiO_3) as secondary minerals. As both quartz and plagioclase lack Mg, the sample was excluded from further studies. (Appendix B Fig. k) TALVIML is a very fine-grained black schist with banded sills of pyrite. Primary minerals are quartz and biotite. Secondary minerals are pyrite, muscovite and plagioclase. This sample was excluded from further studies because its primary minerals contain none or very low amounts of Mg. (Appendix B. Fig. l)

2.2. Tailings

Originally four mine tailings were sampled for the study. They came from Hitura (HITR), Kevitsa (KEVR), Mondo Minerals and Pampalo. It was not possible to include Talvivaara mine to the study on tailings as their method of ore enrichment is bioleaching, which does not produce tailings. Mondo Minerals-tailing contains 75-80% magnesite, why it was excluded from further studies. Pampalo-tailing was also excluded from further studies based on its low Mg-content (5,38 %). As the origin of the further studied tailings HITR and KEVR are rocks from Hitura and Kevitsa mines, it was possible to compare the tailings with pure rocks from the sites in order to see how much the ore enrichment influences the suitability for CCM.

Hitura and Kevitsa mines use selective flotation for ore enrichment. During this process chemicals (such as xanthate salts, sulfuric acid and tall oil) are combined with the ground ore rock and the material gets depleted in ore metals. This changes the overall composition of the original ore rock material as the metals are extracted and various chemicals added.

The tailings have not been studied before for the purpose of CO_2 mineralisation.

3. Methods and Experimental work

3.1. Preliminary mineralogical studies

The mineralogy and texture of each sample was determined with optic microscope from thin sections, different mineral phases were studied with X-ray Diffraction (XRD), chemical compositions were determined with X-ray Fluorescence (XRF), sample surfaces were analysed with Scanning Electron Microscope (SEM) and LOI-values (Loss of Ignition) were measured.

3.2. Experimental work

Rocks were crushed, ground and sieved to fractions $<74 \mu\text{m}$, $75 - 124 \mu\text{m}$, $125 - 249 \mu\text{m}$ and $>250 \mu\text{m}$. Particle size fraction used for all experiments was $75 - 124 \mu\text{m}$ (after [5]).

Experiments were conducted according to the "ÅA Route" (Figure 1). In the first stage, 40 g of each sample was placed in a rotary oven to react with 60 g ammonium sulphate ($[\text{NH}_4]_2\text{SO}_4$) for 30 minutes. The reaction product was dissolved in 500 ml distilled H_2O and insoluble material was filtered out. pH of the remaining liquid was carefully raised by adding ammonium hydroxide (NH_4OH) whereupon solid hydroxides were precipitated. First hydroxide to precipitate is goethite ($\text{FeO}[\text{OH}]$) at pH $\sim 8,5$ and the second is magnesium hydroxide, brucite, ($\text{Mg}[\text{OH}]_2$) at pH $\sim 11,5$. [3] In the second stage the brucite from the first reaction was reacted with CO_2 in an exothermic reaction to form a stable carbonate, magnesite ($\text{Mg}(\text{CO}_3)$). This was done both in a pressurized fluidised bed [5] and through wet carbonation [6]. Extraction experiments on each sample were conducted in two temperatures, 440°C and 480°C (after [7]), to monitor the reactivity differences

caused by increased temperature. Carbonation by two different methods, “wet”/cold or “dry”/hot (as in Figure 1), was done in order to find the ideal way to execute the carbonation.

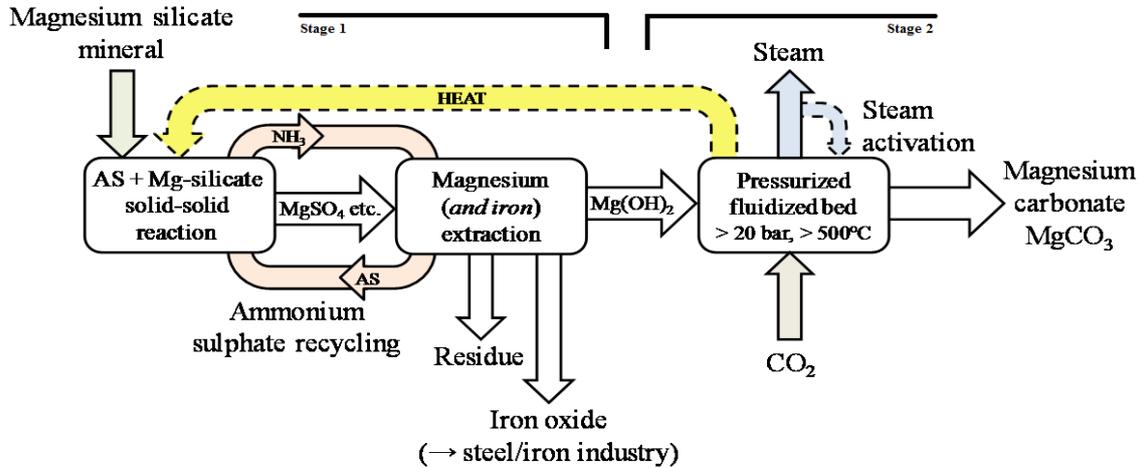


Figure 1. Process scheme for $Mg(OH)_2$ extraction and $MgCO_3$ production. Extraction and precipitation of magnesium at stage 1 is done with ammonia, which is collected afterwards as ammonium sulphate for re-use. Carbonation of precipitated $Mg(OH)_2$ is done in a pressurized fluidized bed at stage 2. Heat energy from stage 2 can be utilized for the extraction process at stage 1. Modified after [8].

The rate of carbonation was determined with the gasometric carbonation analysis method [5]. The rate was calculated by measuring the amount of released gas as the carbonated sample was set to react with 6M HCl. System was calibrated with pure synthetic $MgCO_3$.

4. Results and discussion

4.1. Rock material

Samples were stated successful when they produced sufficient amounts of Mg in relation to their original Mg-content. Their LOI-value over 2,5 % (Figure 2), original Mg-% was >17 % (Figure 3). Samples stated as unsuccessful did not make these grades.

Successful samples were all minerals part of the phyllosilicate group while the unsuccessful samples were minerals of other silicate groups.

Extraction experiments done at higher temperature (480 °C) were in general more successful than the ones done in lower temperature (440 °C). The differences in results were not very large. For unsuccessful samples temperature influence was reversed which may be caused by the Mg/Fe-ratio; higher Fe-rate required more precipitation and higher pH in order to precipitate all Fe and large amounts of Mg was precipitated and filtered out in the process.

Serpentinities from different mines gave good comparable results and showed that the geological location was not a factor. Despite the grade of weathering, all the samples gave good results without large variation. Therefore it can be stated that serpentinities does not need to be fresh in order to be suitable for carbonation.

Chlorite-talc schist did not contain high amounts of Mg but the Mg that was present gave the highest extraction-%. Serpentinities contain high amounts of Mg but it cannot be extracted as easily as from chlorite-talc schists. In a large scale, a rock with relatively low Mg-% can therefore become as profitable as a rock with high Mg-%.

The mineralogical study showed that the olivine-pyroxenite (KEV1) did not contain any olivine, being solely pyroxenes. Based on KEV1-results it can be stated that pyroxenes are not suitable for mineral carbonation.

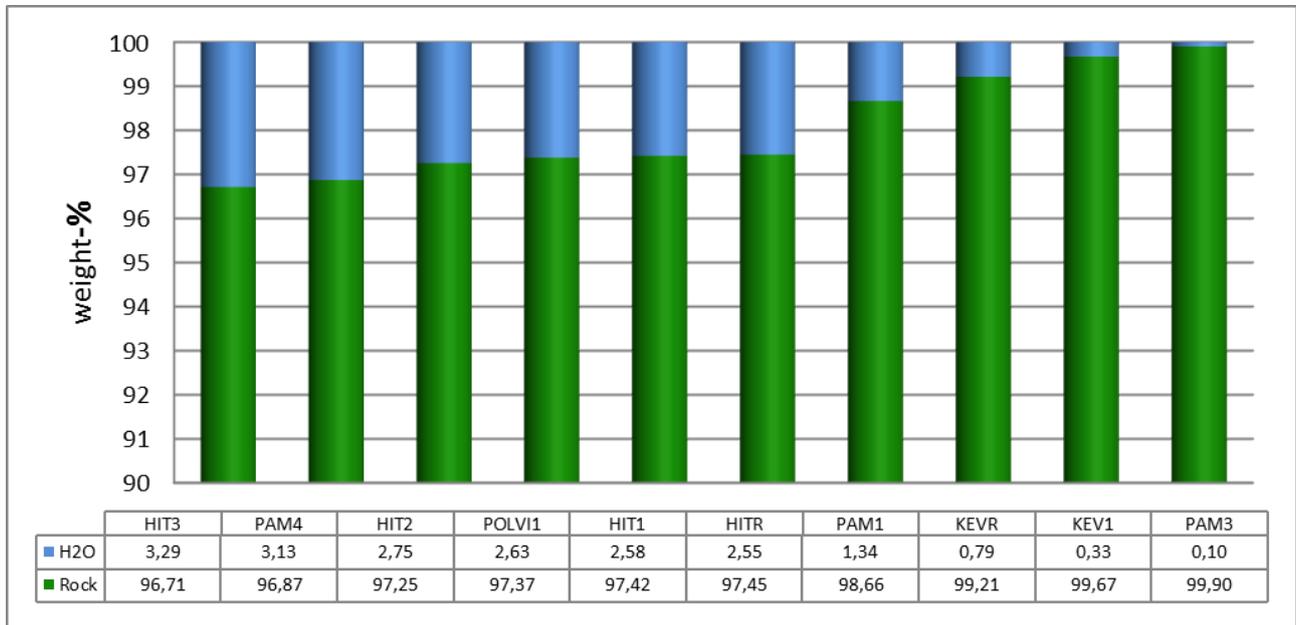


Figure 2. Amount of crystallisation H₂O in studied material. Measurements were made by measuring LOI of the study materials.

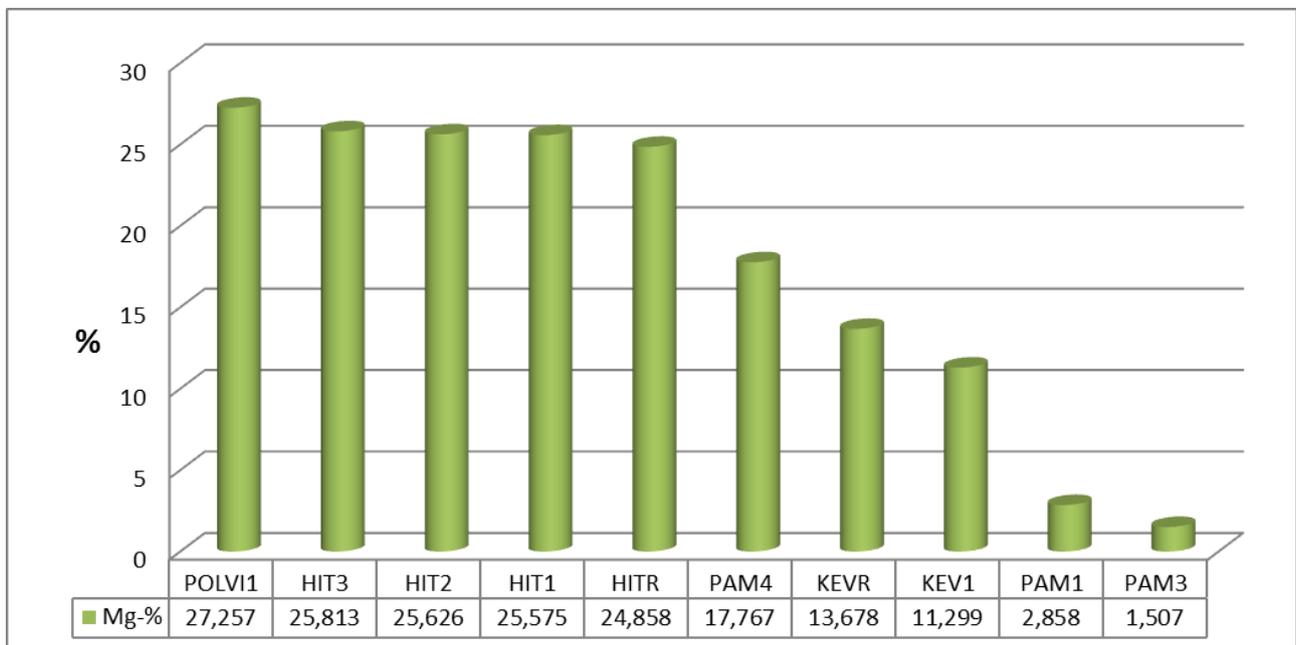


Figure 3. Amount of magnesium in the studied samples (XRF-measurements).

4.2. Tailings

Only HITR-sample was stated as a successful sample. Successfulness was stated based on the same definition as for rock materials: LOI-value being over 2,5 % and original Mg-% being >17 % (Figures 2 and 3). KEVR did not make the grade. It presented a low Mg-content (as did the original rock) (Figure 3) and the amount of the precipitated end product was small (Figure 4) and contaminated by Fe.

It turned out that there were no significant differences in the amounts of Mg-extraction or precipitation between tailings and their host rocks at higher temperature (480 °C). In lower temperature (440 °C) the extraction of Mg was very low for HITR (Figure 4). As the other serpentinite-based samples also presented lower values in lower temperature, a lower value was expected also for tailings. Yet the difference for HITR is unexpectedly low. No fault in method or other error that would cause such a difference was detected and therefore the result is presented as it is.

A notable significant difference between rocks and tailings was the visible chemical intensity during the extraction and precipitation processes of the tailings. Chemical reactions between ore processing solvents apparently present in the tailings and ammonium sulphate during heating in the Mg-extraction stage resulted in unexpected generation of unknown gases that most probably were generated by reactions between the ammonium sulphate and some unidentified species coating the tailing grains. This disturbance was also noticeable in the precipitation stage of the experiment.

In general Fe and Mg were extracted easier from tailings than from rocks. Precipitation of goethite was more efficient in the tailings compared to the rocks and the Fe-contamination in the end product (brucite) was therefore lower. On the other hand, larger amounts of Mg precipitated together with Fe at pH 9 (Mg should be precipitated as Mg(OH)₂ at pH 11,5, see Table 2). The consequence was that less Mg was left to be precipitated and collected subsequently after Fe-species were filtered out. Therefore the extraction values for tailings remain low (Figure 4).

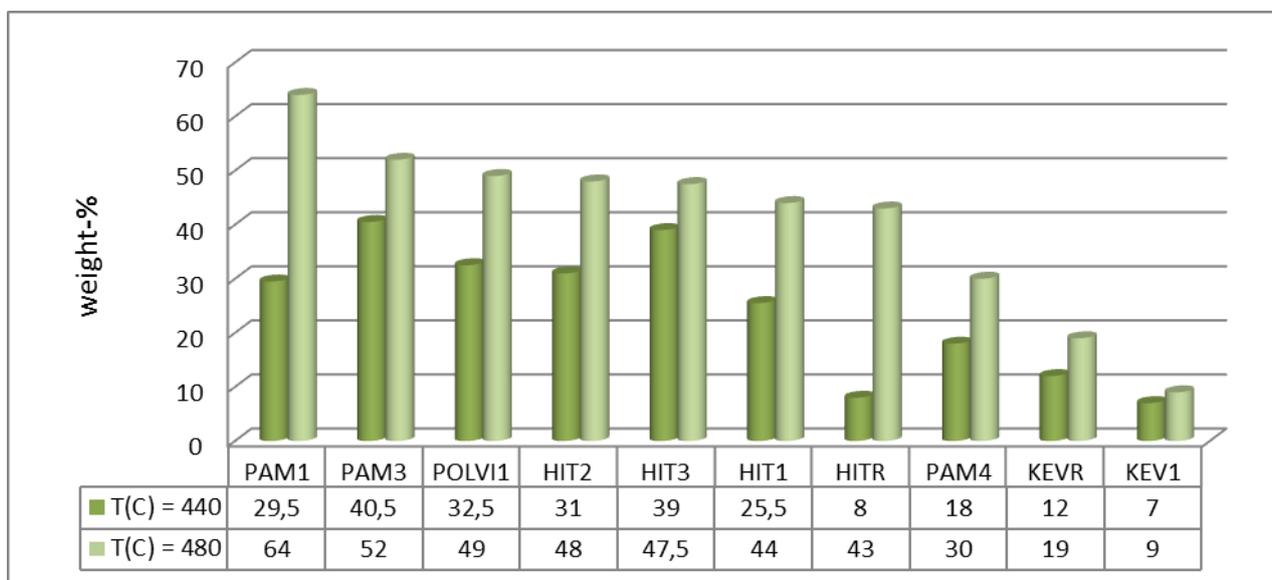


Figure 4. Percentage of extracted magnesium from whole rock material.

Table 2. Mg-analyses (ICP-OES) from liquid before, during and after precipitation of goethite and brucite. Liquid 1 has a pH ~2, liquid 2 has a pH ~9 and liquid 3 has a pH ~11,5. Amount of Mg is shown as mg/l. Liquid 1 shows the amount of Mg after AS extraction (i.e. the amount of Mg extracted from the starting material), liquid 2 shows the amount of Mg after Fe was precipitated as goethite and liquid 3 shows the amount of Mg after Mg was precipitated as brucite.

Sample	Liquid	pH	T=440 °C	T=440 °C	T=480 °C	T=480 °C
			Mg (mg/L)	Mg-prec (%)	Mg (mg/L)	Mg-prec (%)
HIT1	1	~2	5212	100	8974	100
	2	~9	4450	85,38	8768	97,7
	3	~11,5	143	2,74	622	6,93
HIT2	1	~2	6358	100	9790	100
	2	~9	-	-	8920	91,11
	3	~11,5	257	4,04	1033	10,585
HIT3	1	~2	8014	100	9802	100
	2	~9	7656	95,53	9274	94,61
	3	~11,5	345	4,3	482	4,92
KEV1	1	~2	613	100	803	100
	2	~9	569	92,82	641	79,83
	3	~11,5	174	28,38	243	30,26
PAM1	1	~2	677	100	1464	100
	2	~9	508	75,04	533	36,41
	3	~11,5	143	21,12	321	21,93
PAM3	1	~2	489	100	626	100
	2	~9	383	78,32	174	27,8
	3	~11,5	101	20,65	38	6,07
PAM4	1	~2	2590	100	4240	100
	2	~9	2216	85,56	3326	78,44
	3	~11,5	235	9,07	232	5,47
POLVI1	1	~2	7084	100	10696	100
	2	~9	6148	86,79	10352	96,78
	3	~11,5	472	6,66	779	7,28
HITR	1	~2	1621	100	8543	100
	2	~9	1303	79,89	8048	94,2
	3	~11,5	49	3,00	470	5,5
KEVR	1	~2	1355	100	2060	100
	2	~9	1197	88,34	1998	96,99
	3	~11,5	268	19,75	575	27,91

4.3. The role of crystallisation H₂O in the samples and the amount of magnesium in a successful extraction

The amount of crystallisation H₂O in the samples has an effect on the Mg-extraction. “Wet” minerals have higher extraction-% than “dry” minerals [7]. Our studied samples contained varying amounts of H₂O in their lattices (Figure 2) and the results gained in this study are congruent with results from previous studies [2][5].

It is the amount of Mg in the starting material and how easily Mg is extracted from it that gives the optimal results for CCM. The studied material can be divided in more successful samples and unsuccessful samples depending on their initial Mg-content (Figure 3) and the Mg-extraction-% (Figure 4). Mg-extraction-% was determined by calculating the amount of Mg (in grams) in the original 40 g rock sample (based on the XRF-results) and subtracting the amount of Mg (in grams) in the first liquid sample (g/L) (Table 2). Based on the difference between the values it was possible to calculate how many percents were left in the insoluble material and how much ended up in the low-pH liquid, ready to be precipitated. Successful samples, serpentinites and a talc-chlorite schist, contained ~2,5 – 3,3 % crystallisation H₂O (based on Loss of Ignition tests, LOI) and more than 17 % Mg (17 – 27 %). Unsuccessful samples contained 0,1 – 1,3 % crystallisation H₂O and 1 - 13 % Mg. The unsuccessful samples were the olivine-pyroxenite from Kevitsa, the iron formation from and the andesite-tuff from Pampalo.

According to these results a pattern can be noted; a successful material for carbonation needs to consist of >17 % Mg and it needs to contain > 2,5 % crystallisation H₂O. When samples PAM4 and POLVII are compared, both are categorized as successful but PAM4 contains 3,13 % crystallisation H₂O and 17,7 % Mg while POLVII contains 2,63 % crystallisation H₂O and 27,3 % Mg. These factors seem to balance each other. Determining the ratio at which they balance each other needs further studying.

4.4. The difference between theoretical and actual extraction of magnesium

Differences between the theoretical maximum and actual amounts of Mg extracted from mine waste are significant (Figures 5a, 5b). As all the recovered Mg was carefully collected it was obvious that all Mg in the starting material was not extracted during heating with AS in the rotary oven. This means that the unextracted Mg of the starting material was filtered off as “unreacted” with other insoluble materials and removed from the process before the precipitation of brucite was started. Figure 4 shows (in weight-%) how much Mg was extracted altogether from the starting material. ICP-OES-analysis on precipitation liquids verify that extracted Mg was successfully precipitated during the process and did not remain in high-pH liquid [2]. Liquid samples for ICP-OES were collected before anything had been precipitated (~pH 2), after Fe was precipitated and filtered off (~pH 9) and after Mg was precipitated and filtered off (~pH 11,5). This made it possible to closely follow the amount of Mg in liquid during the whole precipitation process.

The amount of Mg that was extracted during heating is shown as the value for liquid 1 in [2]. Table 2 also shows how much was left after precipitation of Fe (as goethite) (liquid 2) and how much was left in the final high-pH liquid after precipitation of brucite (liquid 3). Percentages of recovered Mg in relation to the amount of Mg in original low-pH liquid are also presented.

Based on the measured results, the problem lies with the extraction part of the process more than in actual Mg(OH)₂-precipitation. Extracted Mg that is found in the low-pH liquid, is precipitated up to >90 % (Figure 6) but the rate of extraction from the starting materials vary between 7 and 40,5 % at 440°C and between 9 and 64% at 480°C depending on the sample (Figure 4).

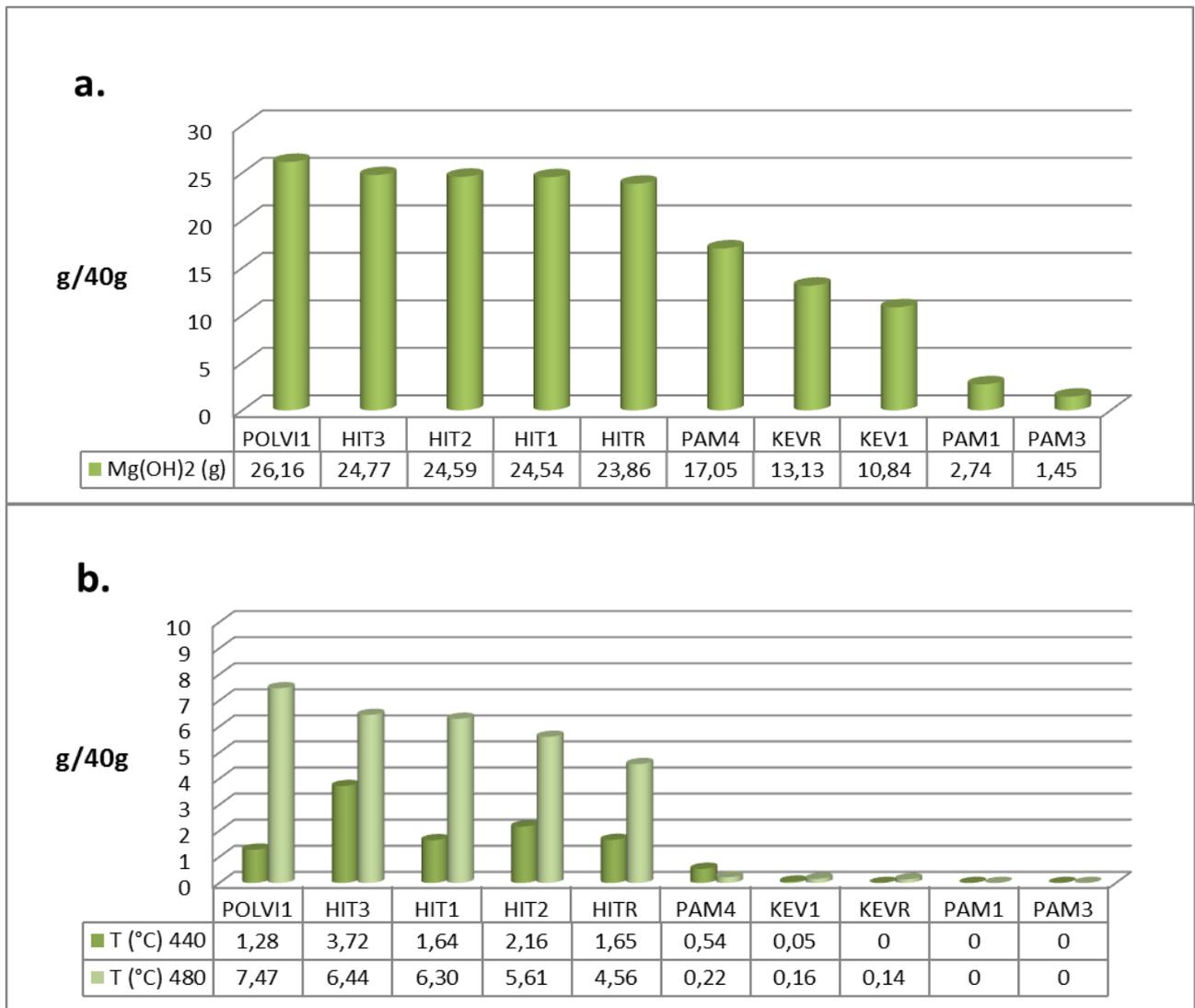


Figure 5a. Calculated theoretical amounts of $Mg(OH)_2$ precipitated from samples (based on ICP-OES and XRF). 5b. Actual measured amounts of precipitated Mg in the form of $Mg(OH)_2$.

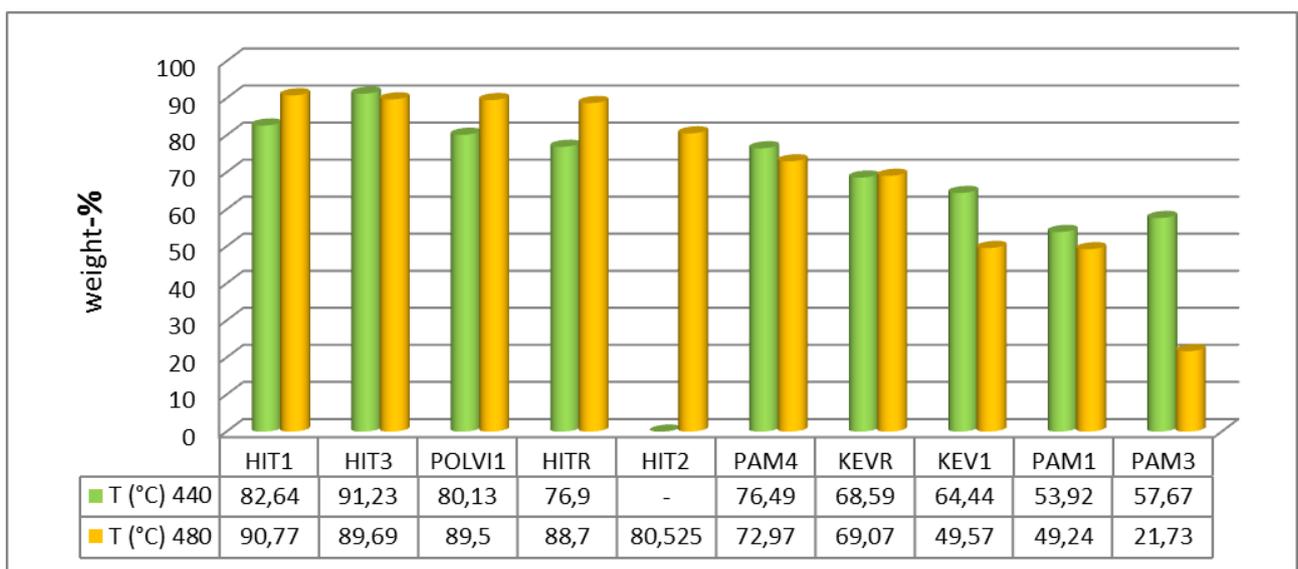


Figure 6. Percentages of precipitated magnesium. Calculations are based on precipitation liquids with ICP-OES. Due to contamination, no data is available for HIT2 T (°C) 440.

Theoretically the Mg is precipitated as $\text{Mg}(\text{OH})_2$, but as [2] states, it can also be precipitated as MgO. MgO (40,31 g/mol) is lighter than $\text{Mg}(\text{OH})_2$ (58,33 g/mol), which could partly explain the weight difference in theoretical $\text{Mg}(\text{OH})_2$ precipitation and the actual precipitated product. In section “4.5 Carbonation” it is pointed out that using XRD both $\text{Mg}(\text{OH})_2$ and MgO were detected together with MgCO_3 . Unless all the MgO was formed during carbonation process, it has formed when $\text{Mg}(\text{OH})_2$ was supposed to precipitate. This is though unlikely. Therefore the precipitated products consist of unknown ratios of MgO and $\text{Mg}(\text{OH})_2$ (XRD results from precipitates were not quantitative enough to be used for exact determination). Having MgO instead of $\text{Mg}(\text{OH})_2$ results in a lower weight in the precipitated end product.

4.5. Carbonation

The grade of carbonation in a pressurized fluidized bed and through wet carbonation were studied on XRD (after [5]) in order to see how much of the brucite had been converted into MgCO_3 . According to the peaks detected by XRD the product consisted of MgCO_3 , $\text{Mg}(\text{OH})_2$ and MgO but exact ratios were unclear as well as was their actual occurrence, besides amorphous phases. Additional Electron Spectroscopy for Chemical Analysis (ESCA) studies of the end products supported the XRD results but did not either clarify the exact ratios between the phases. Residual amounts of Fe were detected during carbonation process as the material turned yellow or presented a light yellow shade. This was clearly present when carbonation was done through wet carbonation as the sample turned yellow 3 minutes after carbonation was started. Materials carbonated in the pressurized fluidized bed were white after carbonation but as they were heated in order to recrystallize MgCO_3 , they also turned yellow or brown.

The degree of carbonation indicated that the carbonation with the procedure using aqueous solution and CO_2 at ambient conditions had been successful. All the samples gave degrees over 100 % (100,4 – 108,2%). The samples done in 480 °C produced clearer end product compared to the samples done in 440 °C which supports previous results on the optimal temperature. These results need to be considered suggestive more than accurate as only one sample had not been contaminated by Fe. As CO_2 can also form an iron carbonate, siderite, when Fe is present, it can be assumed that some CO_2 was carbonated with Fe instead of Mg. As the measuring system is calibrated for MgCO_3 the percentages for carbonation rate may vary. Despite the inaccuracies, measurements on the carbonation degree show that the carbonation using aqueous solution and CO_2 at ambient conditions is a usable method for this purpose. Even though it was not possible to determine where the CO_2 was bound it was clear that significant amounts of it were present.

4.6. Discussion and additional research

The problem with Fe present in ultramafic rocks could be solved by extracting forms of Fe with other methods. Having Fe present in the extraction process consumes energy [2], therefore removal of magnetite and hematite from the starting material prior to the Mg extraction with AS would decrease the energy costs for the whole extraction process. The difference in density between magnetite ($\rho = 5,21$) and hematite ($\rho = 5,28$) is significant compared to serpentinite ($\rho = 2,56$). Therefore these forms of Fe can possibly be separated through flotation or Wilfley table mineral separation. Separation methods based on density differences between minerals are widely used among geological and mineralogical context because they are relatively cost-effective and easily accessible.

If mine tailings are introduced to mineral carbonation as raw material, it is important to acknowledge their diverse chemical composition. Especially aqueous solutions produced from experiments done with tailings at 480°C reacted strongly with NH_4OH . In some cases the ammonium solution started reacting with fumes from sample liquid when the syringe containing ammonium solution was placed near the fumes (within range of ~10 centimeters). One drop of

ammonium solution was enough to cause the sample liquid to react violently and release a lot of unidentified vapour. Pronounced reaction continued until pH reached 3 and until that, the adding of NH_4OH was done carefully one drop at a time.

The main problem of the carbonation method seems to be the rate of extraction from the raw material. Even though the precipitation and collection of the $\text{Mg}(\text{OH})_2$ is executed successfully, the overall extraction rate remains low when the ammonium salts cannot extract nearly all the Mg from the raw material. Further studies on minerals is needed in order to determine which minerals give off their Mg and what features influence their urge to do so.

Olivine was originally one of the most interesting raw materials. As the presupposed olivine-pyroxenite sample did not contain any olivine, another olivine rock will be introduced to future experiments.

As all the successful samples turned out to be part of the phyllosilicate family, which had not been anticipated, further studies will contain silicates from varying silicate groups in order to confirm the essence of the silicate group.

5. Conclusions

Magnesium rich ultramafic rocks containing minerals of the phyllosilicate group are the most promising raw material for mineral carbonation. Chlorite-talc schist show as profitable results as serpentinite even though the chlorite-talc schist in this study contained less Mg than the serpentinites. Serpentinites can be used as raw material at least 15 years after the rock has been exposed to the atmosphere. A successful raw material consists of >17% Mg and >2,5% of crystallisation H_2O .

Enrichment chemicals present in the tailings can end up in the aqueous solutions.

An extraction temperature of 480 $^\circ\text{C}$ is more favorable than 440 $^\circ\text{C}$.

The carbonation process requires improvements before it can be utilized at mines. Especially extraction efficiency of magnesium (or other desired components) from the raw material needs to be improved before it gives cost-effective amounts of raw material for carbonation. Precipitating the $\text{Mg}(\text{OH})_2$ is successful even though a high content of Fe in material may induce contamination of the end product. Tests with separation of iron oxides prior to Mg extraction are suggested to increase the Mg/Fe proportion in the starting material before extraction and to reduce to problem with iron contamination in the precipitation stage. If parts of the end product can be carbonated (periclase, brucite), this problem is not severe as long as it is noted in further processing.

Mineralogical characteristics have a significant role in successful extraction and carbonation of natural rocks. Differences between rocks and tailings were not significant based on average results. A benefit with tailings is their readily ground state but as they have gone through chemical processing, they contain components that may disturb the precipitation process.

Further studies on suitable rock types and essential characteristics are necessary. Based on this study, further studies are continued on different types of serpentinites, phlogopite, vermiculite, olivine and additional phyllo- and neso/-orthosilicates.

Acknowledgments

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Appendix A

Major element (oxides) analyses (XRF) of the samples used in this study.

	HIT1	HIT2	HIT3	HITR	KEV1	KEVR	PAM1	PAM3	PAM4	POLVI1
SiO₂	38.82	39.34	35.75	37.57	47.23	44.06	39.13	50.85	48.67	44.65
TiO₂	0.02	0.02	0.02	0.05	0.42	0.31	1.83	0.28	0.28	0.05
Al₂O₃	0	0	0	1.09	3.84	2.97	11.74	10.60	5.47	2.33
Fe₂O₃	17.42	16.44	17.21	16.47	11.52	13.11	18.58	27.68	10.02	6.63
MnO	0.15	0.13	0.14	0.19	0.20	0.20	0.41	0.07	0.18	0.06
MgO	42.41	42.49	42.80	41.22	18.74	22.68	4.74	2.50	29.46	45.19
CaO	0.13	0.07	0.23	0.47	16.89	15.17	15.31	4.41	5.25	0.04
Na₂O	0.37	0.45	0.47	0.34	0	0.18	1.87	0	0	0.39
K₂O	0	0	0.01	0.20	0.40	0.18	5.40	3.31	0.02	0
P₂O₅	0	0	0	0	0	0	0.18	0.06	0	0
S	0.11	0.11	0.80	0.94	0.19	0.51	0.25	0	0	0.05
tot.	99.41	99.04	97.42	98.54	99.42	99.36	99.44	99.75	99.36	99.39

Appendix B – Scanning electron microscope images of the rocks used in this research. See text for further explanations.

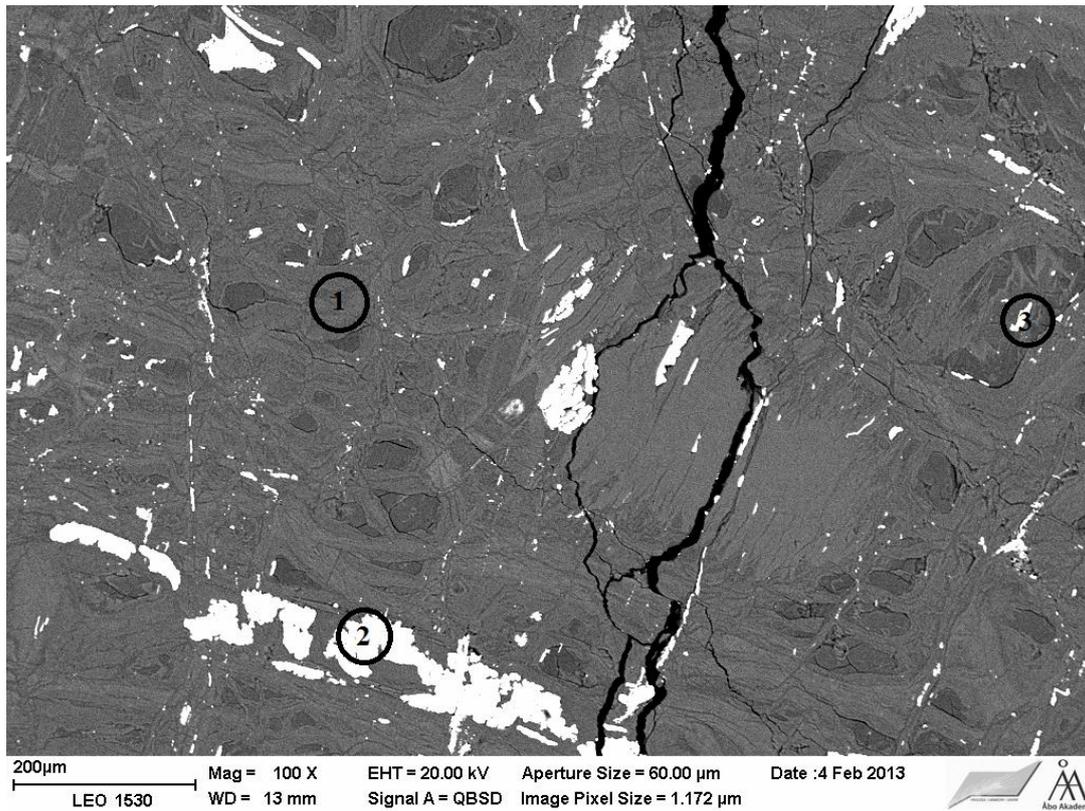


Figure B.a. Sample HIT1. 1=serpentinite, 2= magnetite, 3=pyrite.

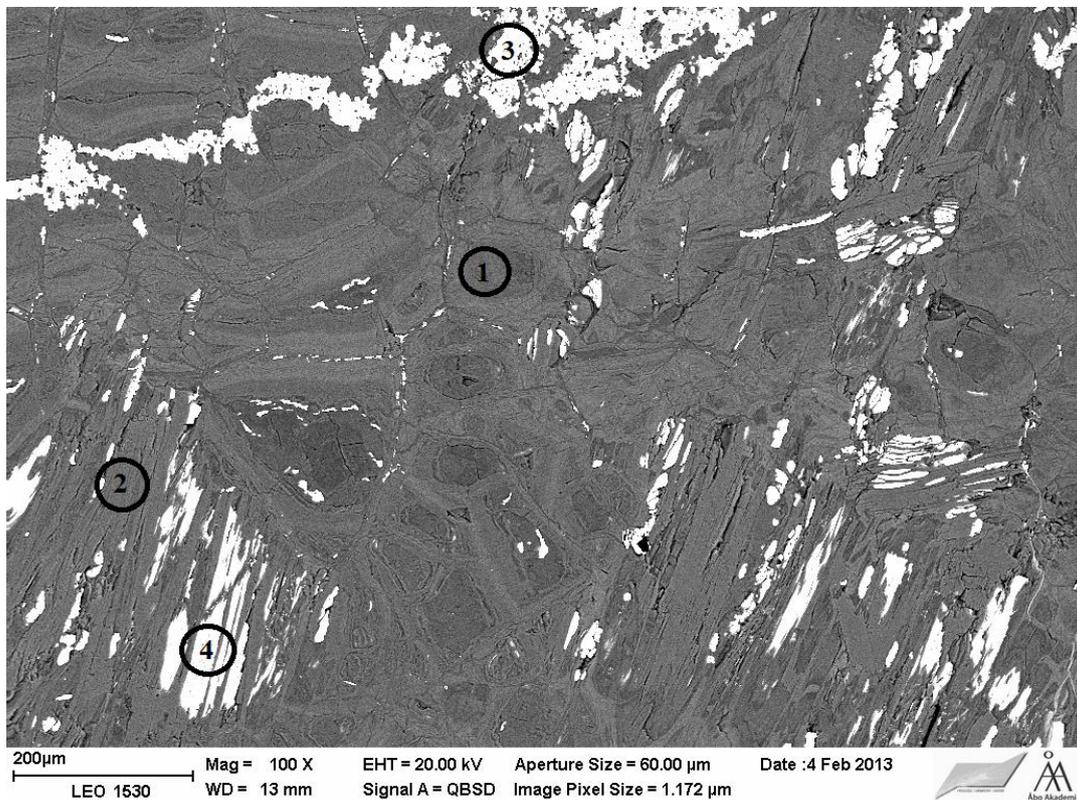


Figure B.b. Sample HIT2. 1=serpentinite, 2=chloritised serpentinite 3= magnetite, 4=pyrite.

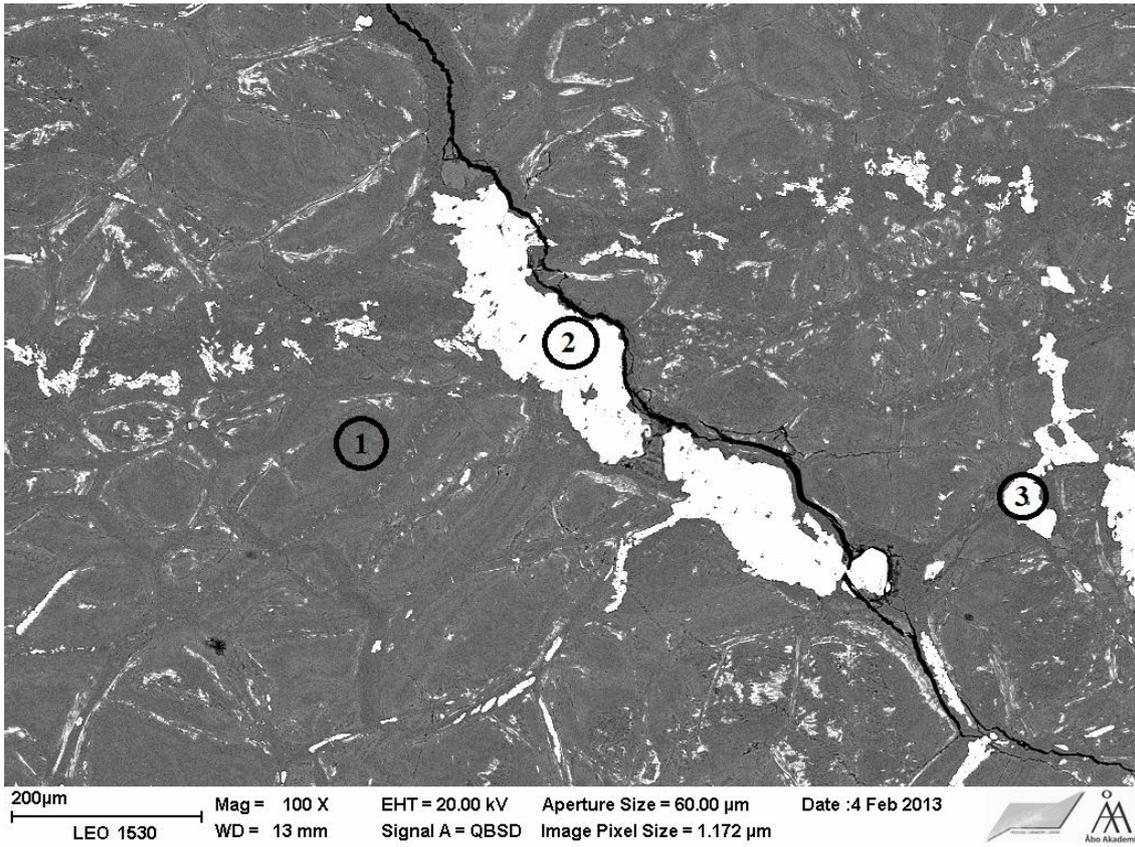


Figure B.c. Sample HIT3. 1=serpentinite, 2= magnetite, 3=pyrite.

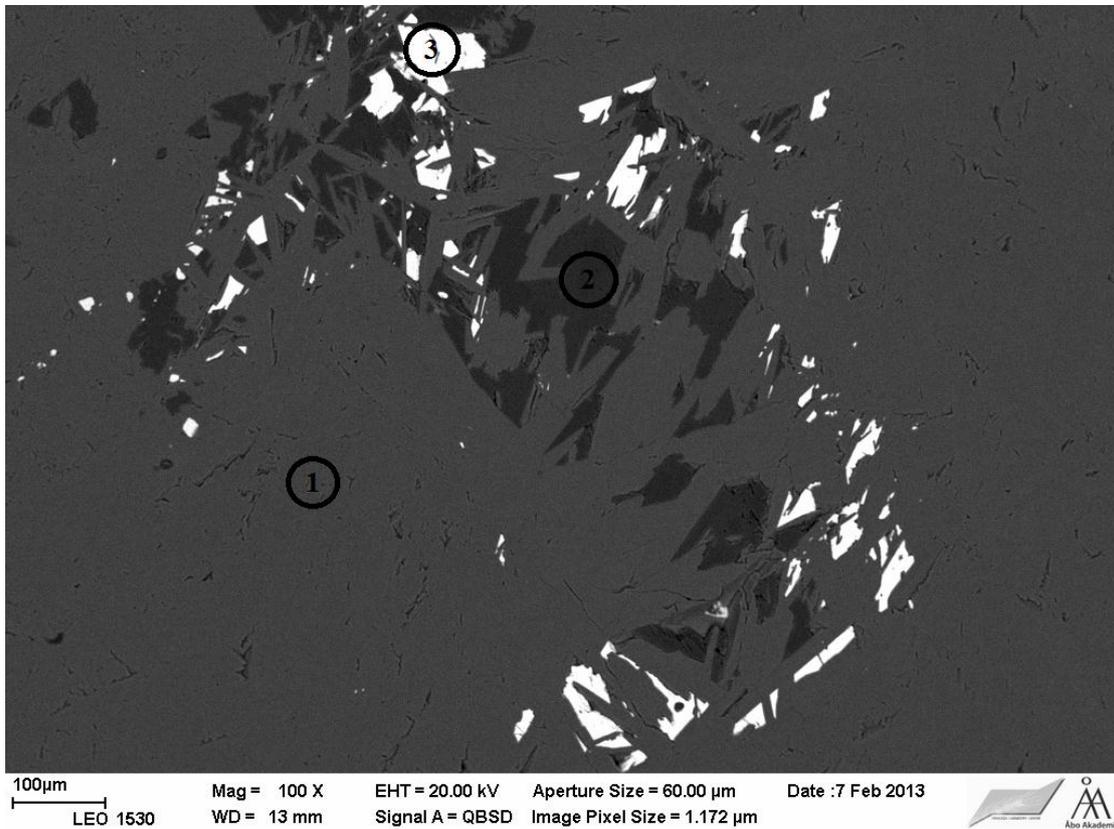


Figure B.d. Sample POLVII. 1=serpentinite, 2= magnesite, 3=pyrite.

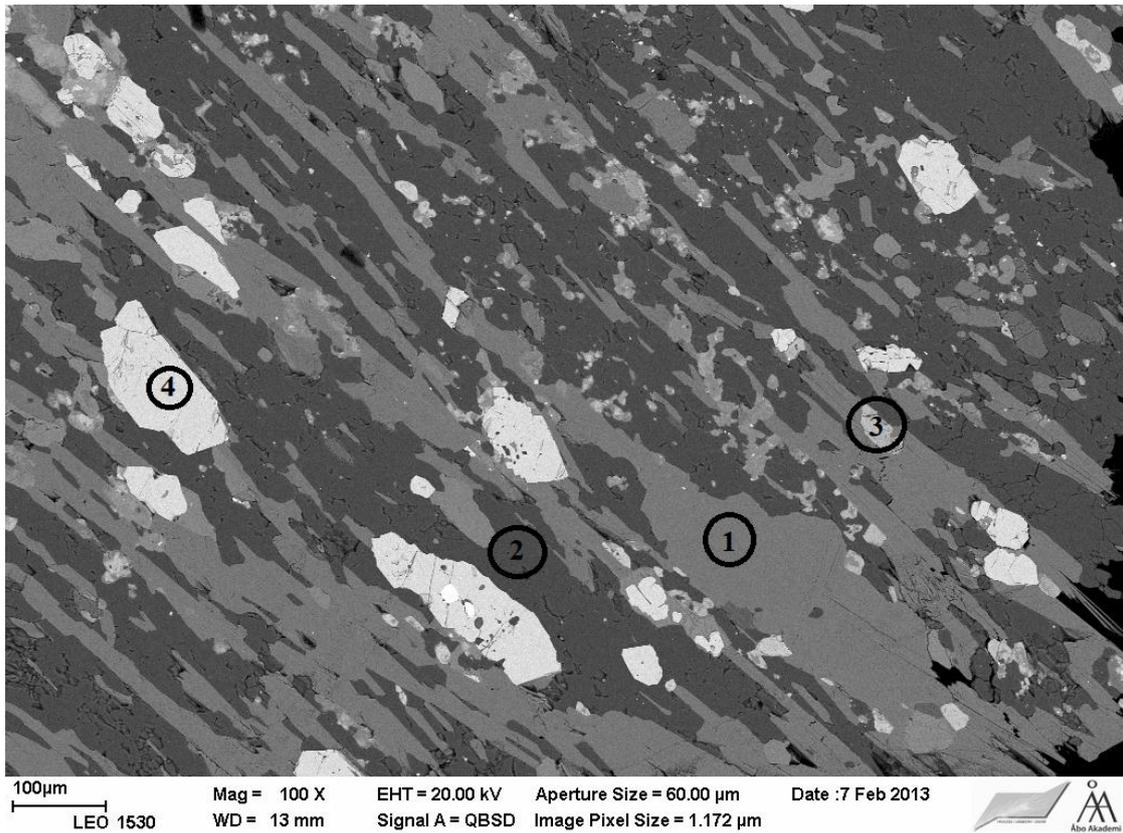


Figure B.e. Sample PAM1. 1=biotite, 2= plagioclase, 3=quartz, 4= iron oxide.

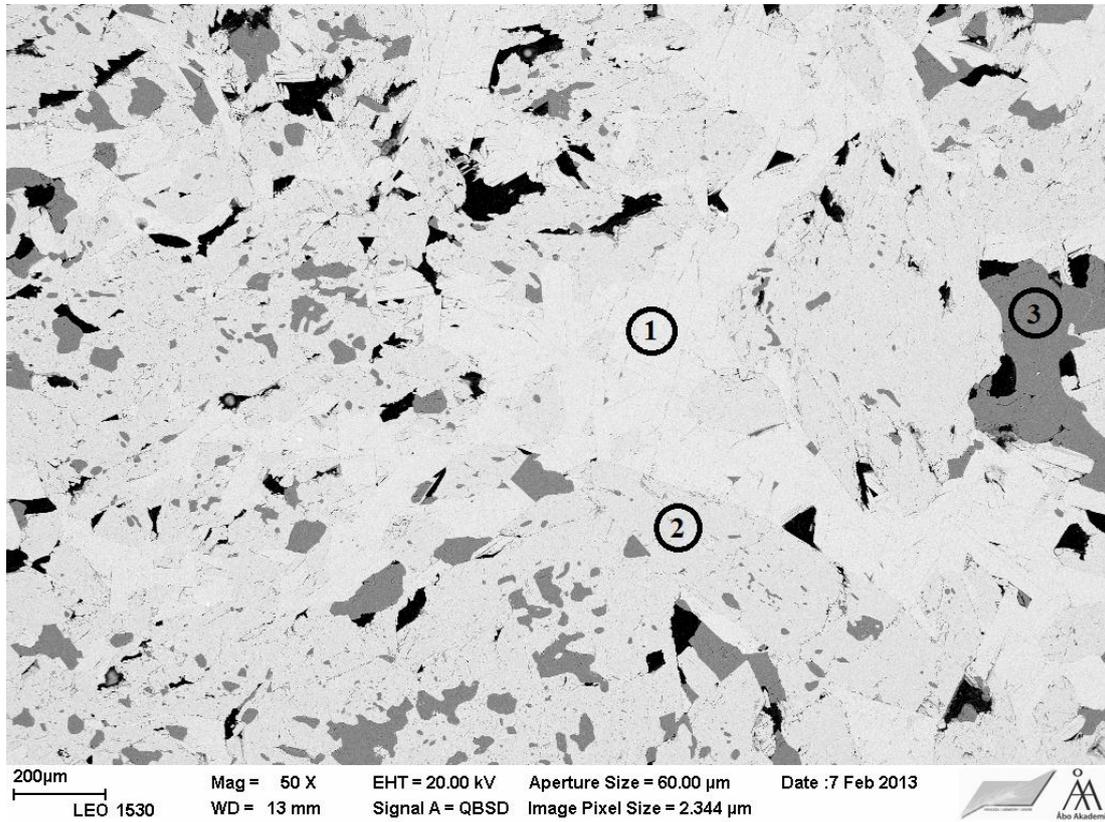


Figure B.f. Sample PAM3. 1=amphibole, 2= stilpnomelane, 3=quartz.

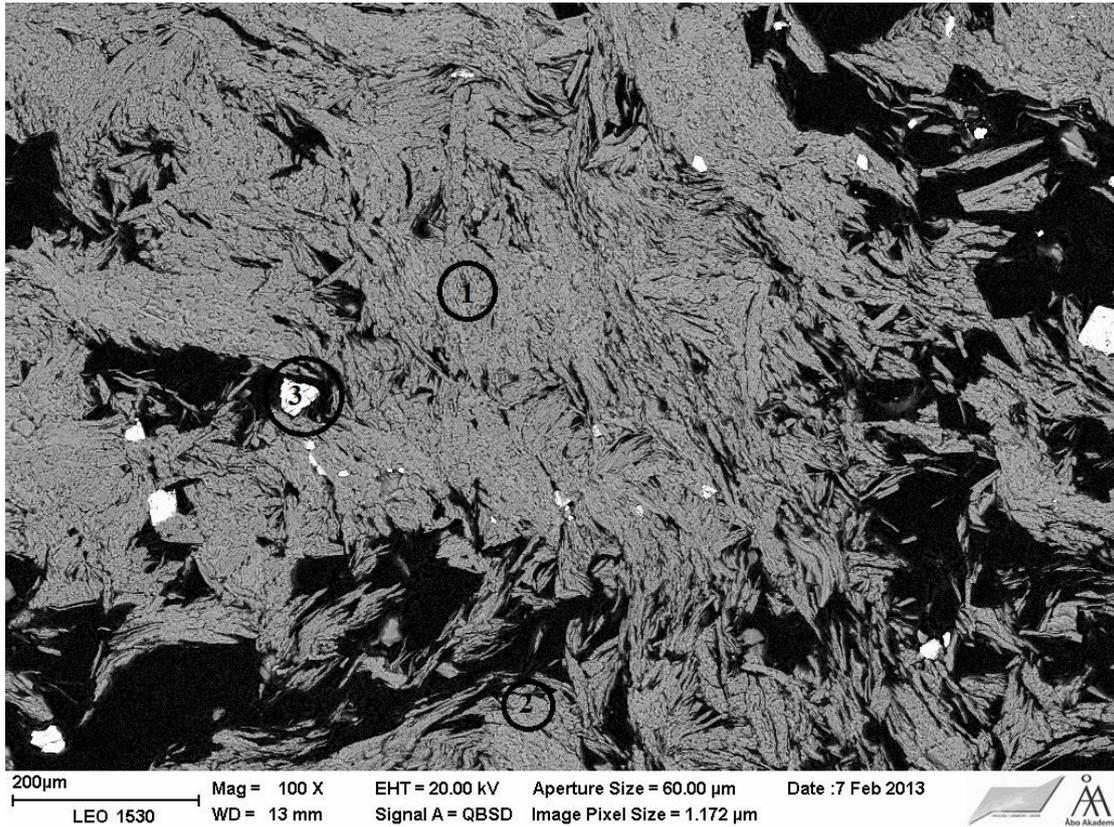


Figure B.g. Sample PAM4. 1=talc, 2= chlorite, 3=pyrite.

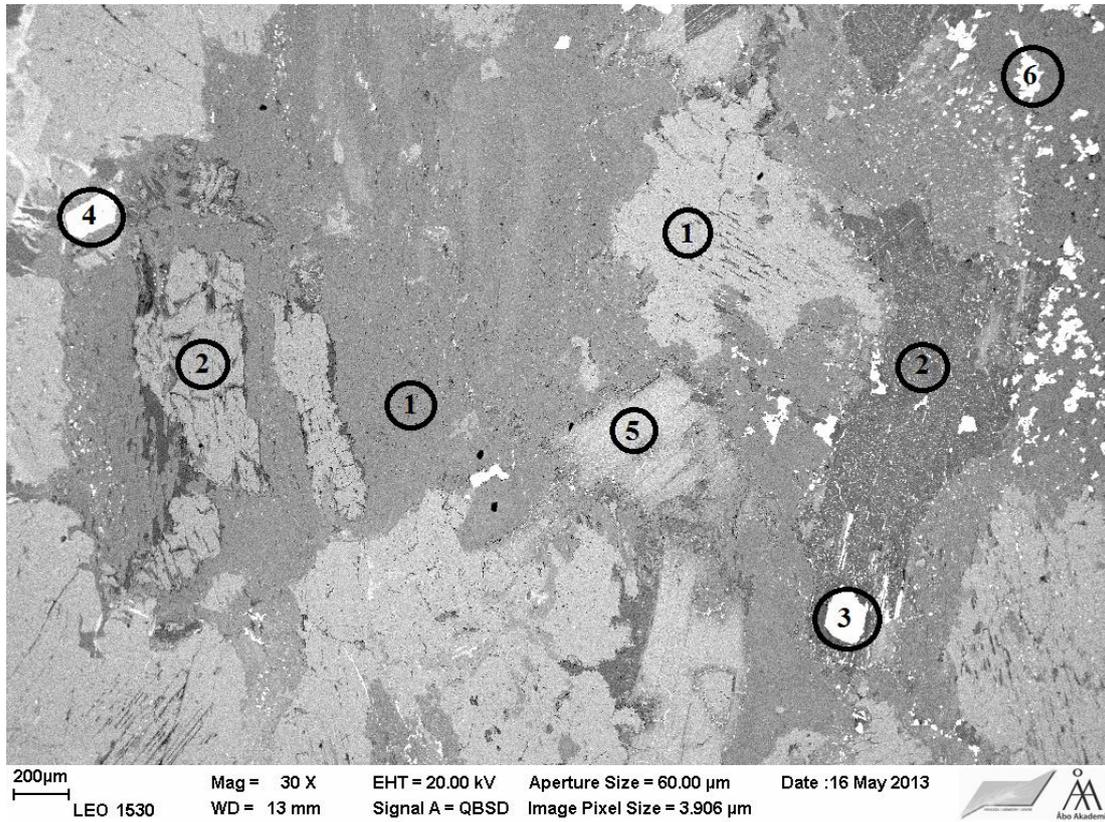


Figure B.h. Sample KEV1. 1=pyroxene, 2= amphibole, 3=pyrite, 4= iron oxide, 5= biotite, 6= magnetite.

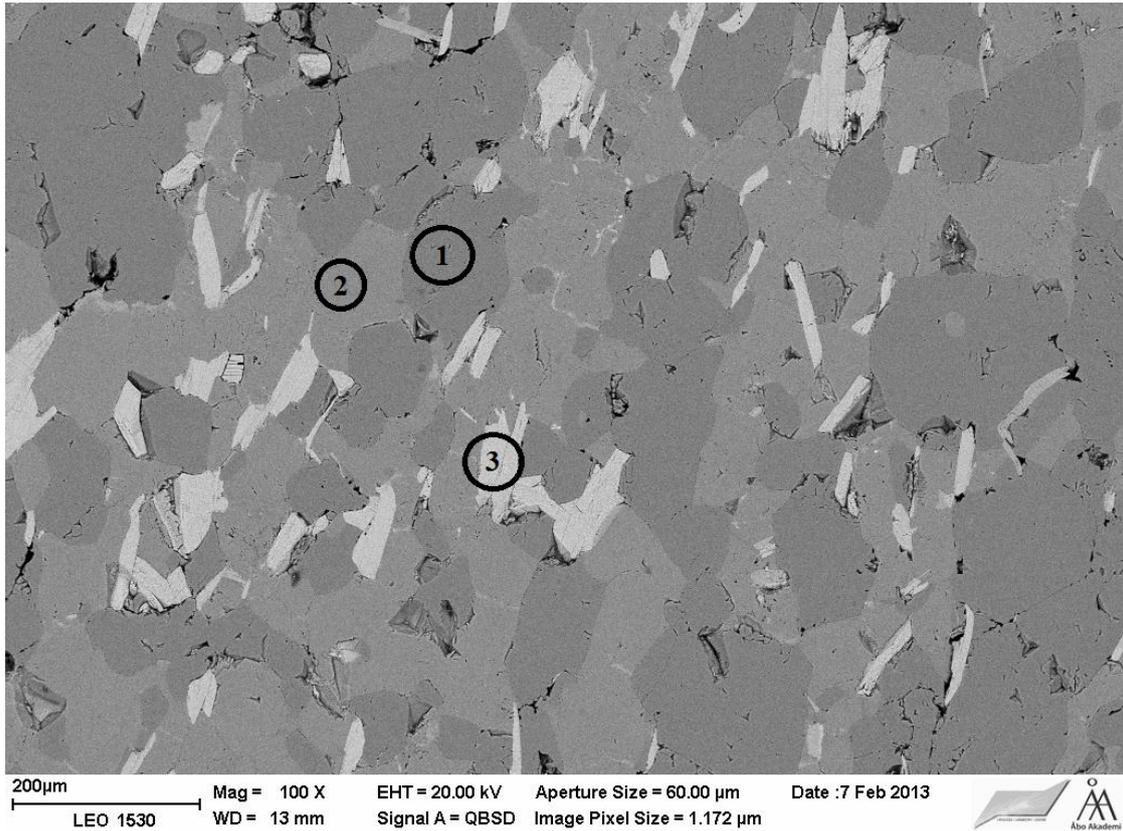


Figure B.i. Sample PAM2. 1=quartz, 2= plagioclase, 3=amphibole.

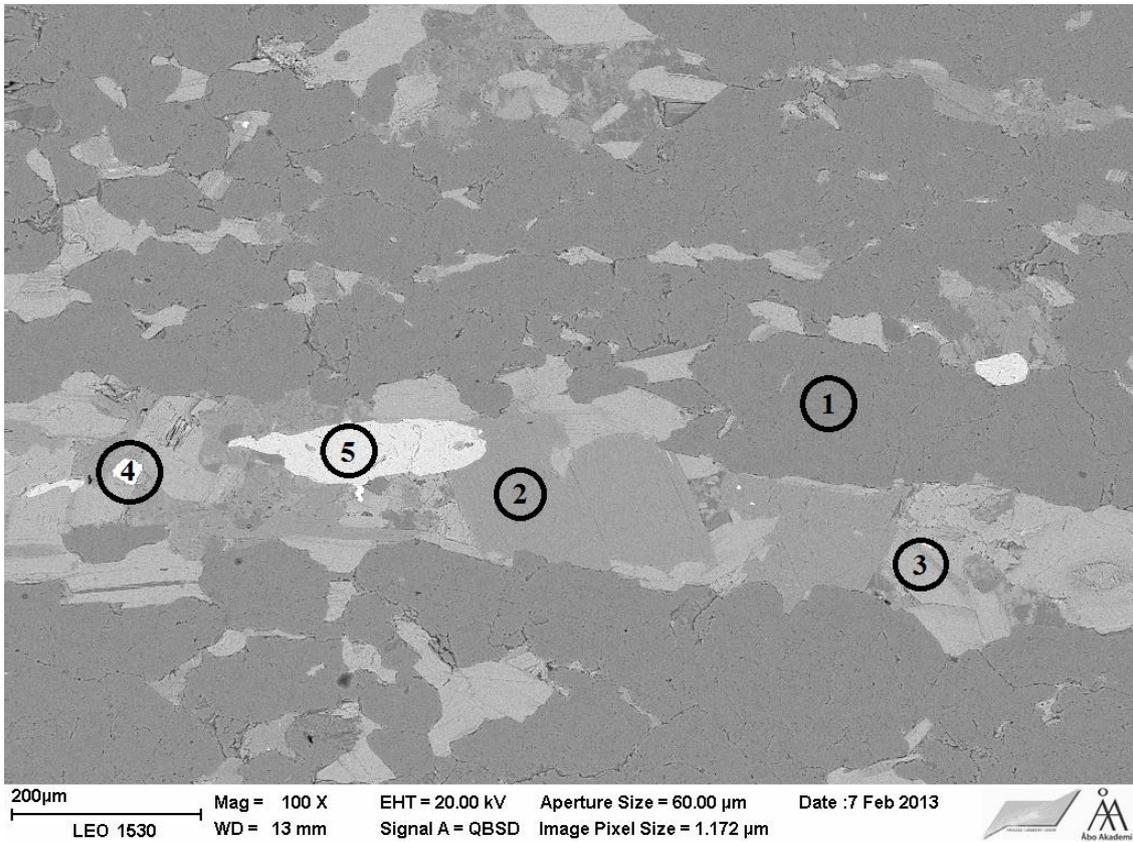


Figure B.j. Sample TALVIQ. 1=quartz, 2= muscovite, 3=biotite, 4= zircon, 5= apatite.

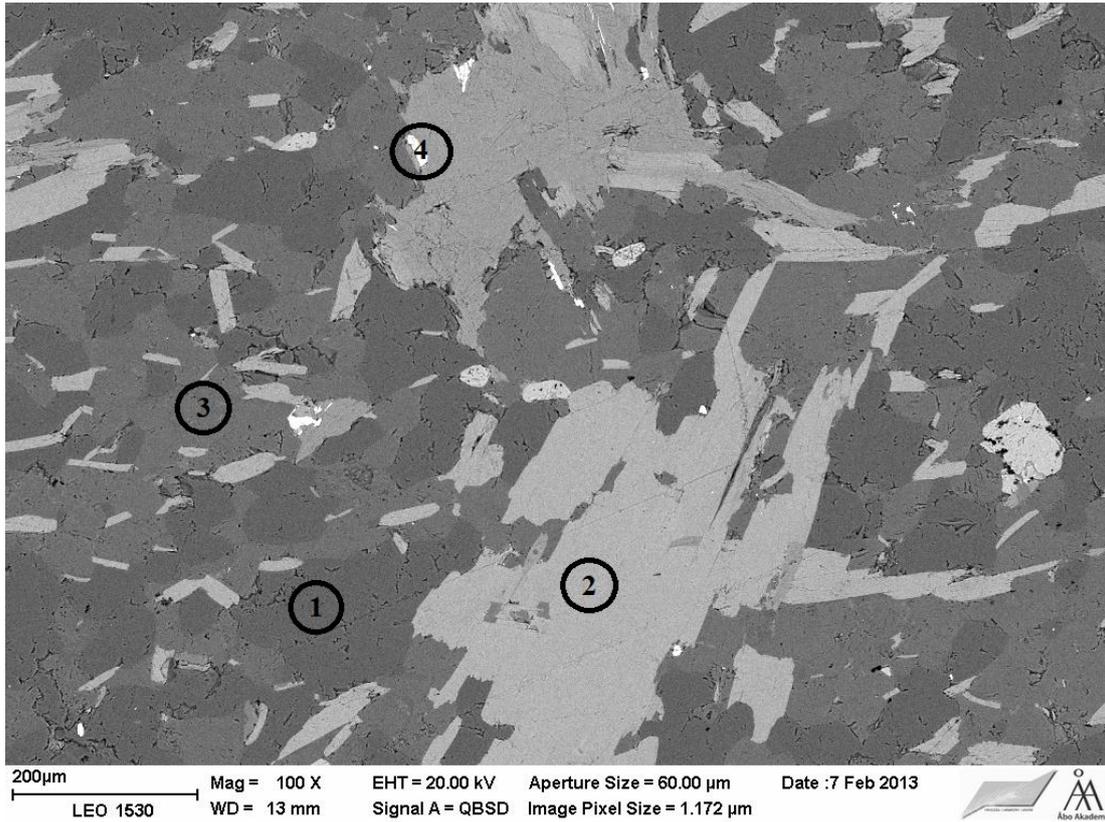


Figure B.k. Sample TALVIKL. 1=quartz, 2=biotite, 3= plagioclase, 4= ilmenite.

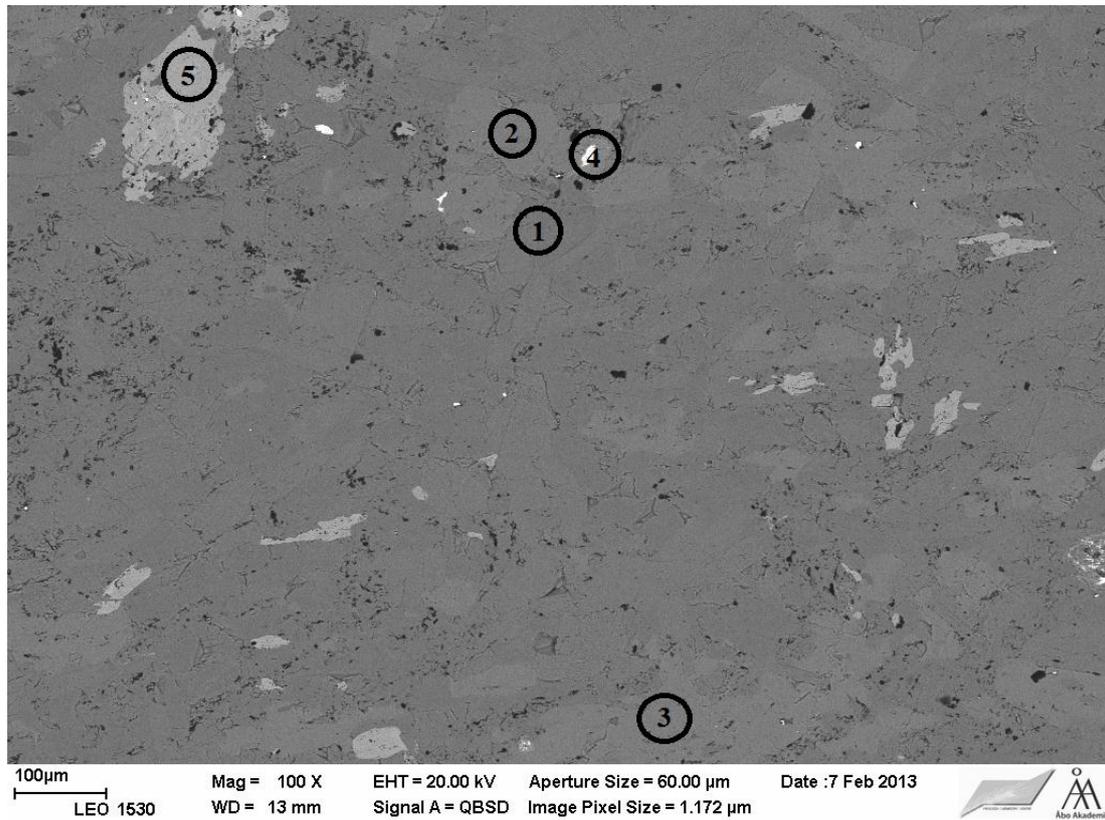


Figure B.l. Sample TALVIML. 1=quartz, 2= biotite, 3= muscovite, 4= pyrite, 5=titanite.

Appendix C – XRD-patterns of the samples stated potential. See further explanations in section 2.

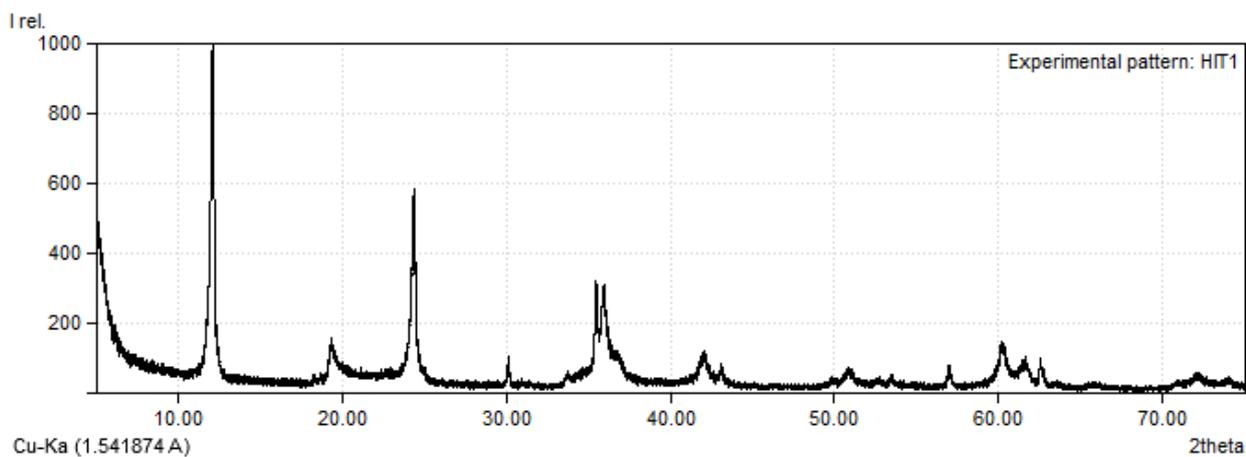


Figure C.a. Sample HIT1.

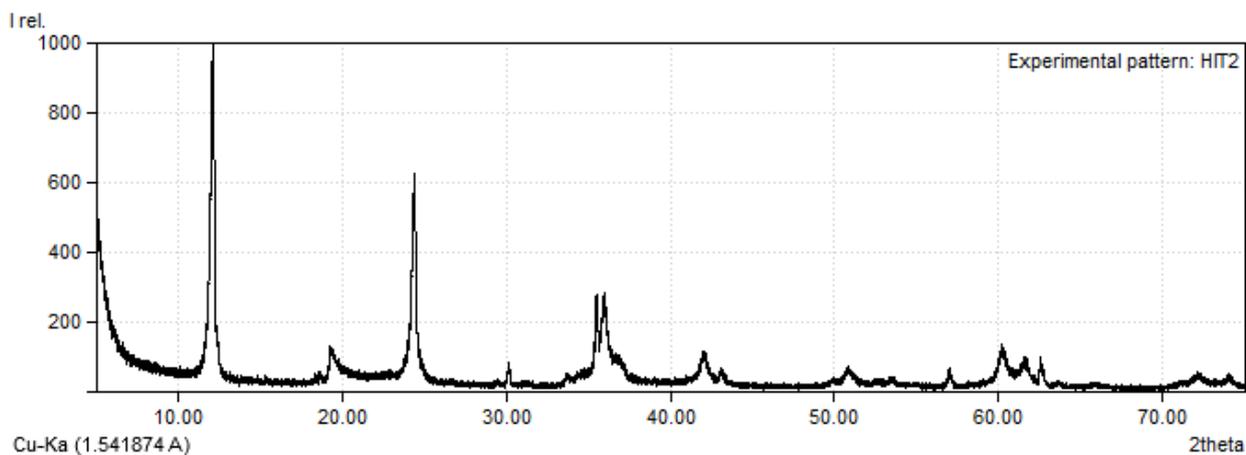


Figure C.b. Sample HIT2.

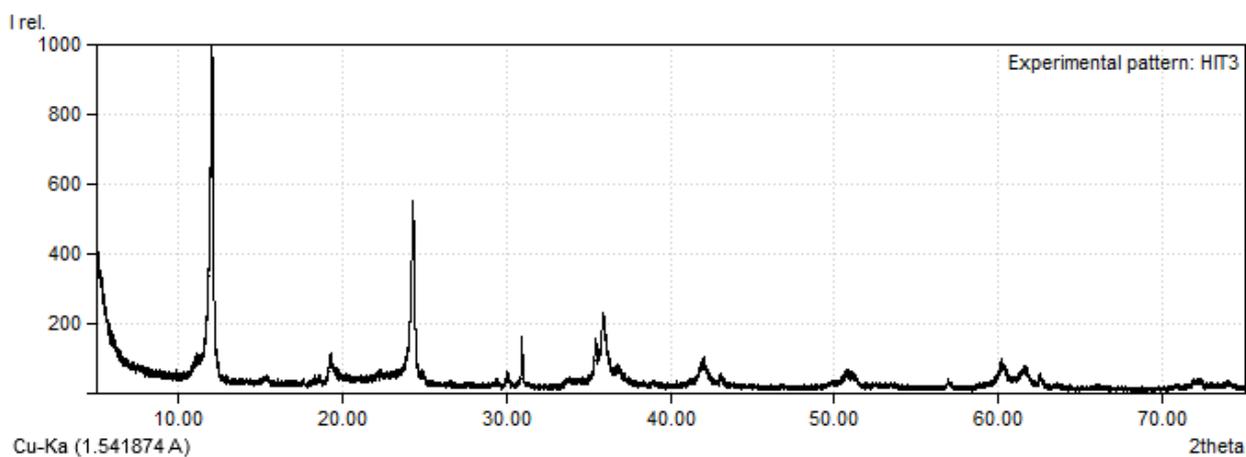


Figure C.c. Sample HIT3.

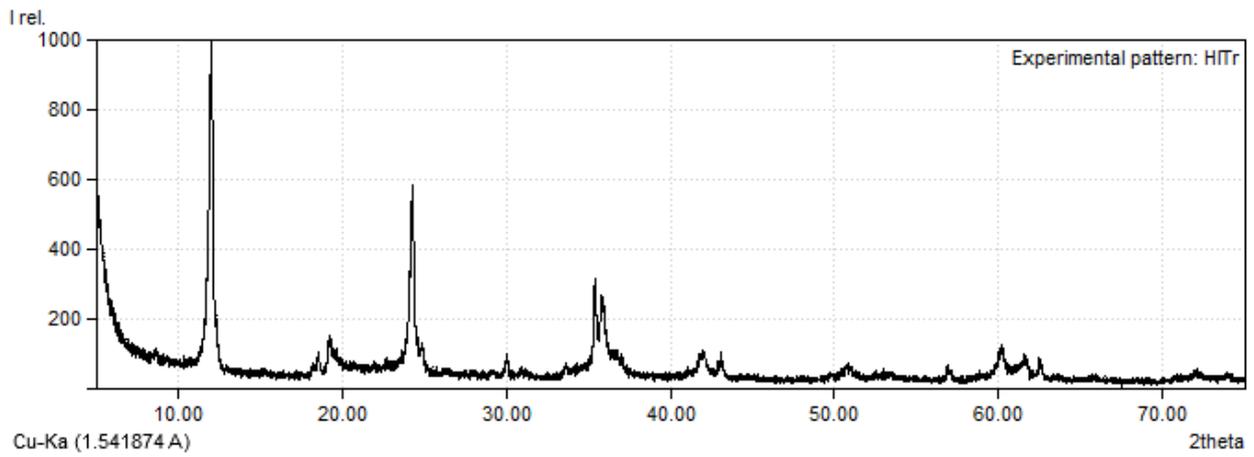


Figure C.d. Sample HITr.

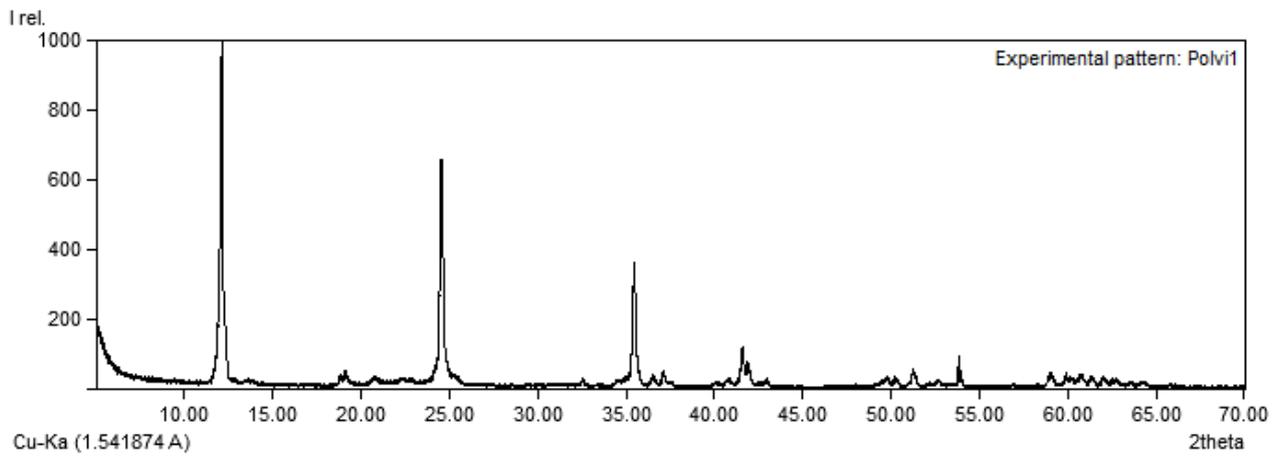


Figure C.e. Sample Polvi1.

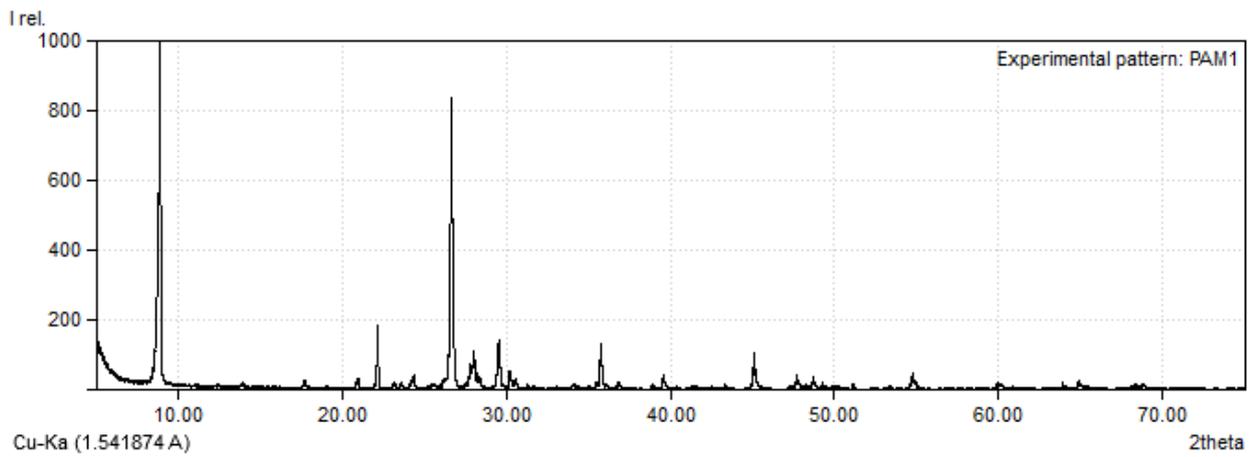


Figure C.f. Sample PAM1.

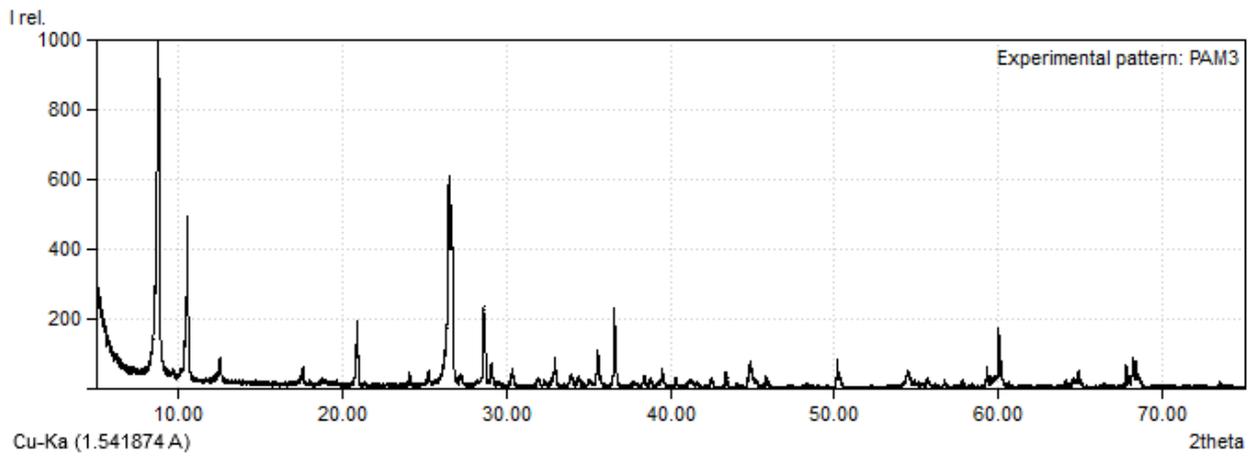


Figure C.g. Sample PAM3.

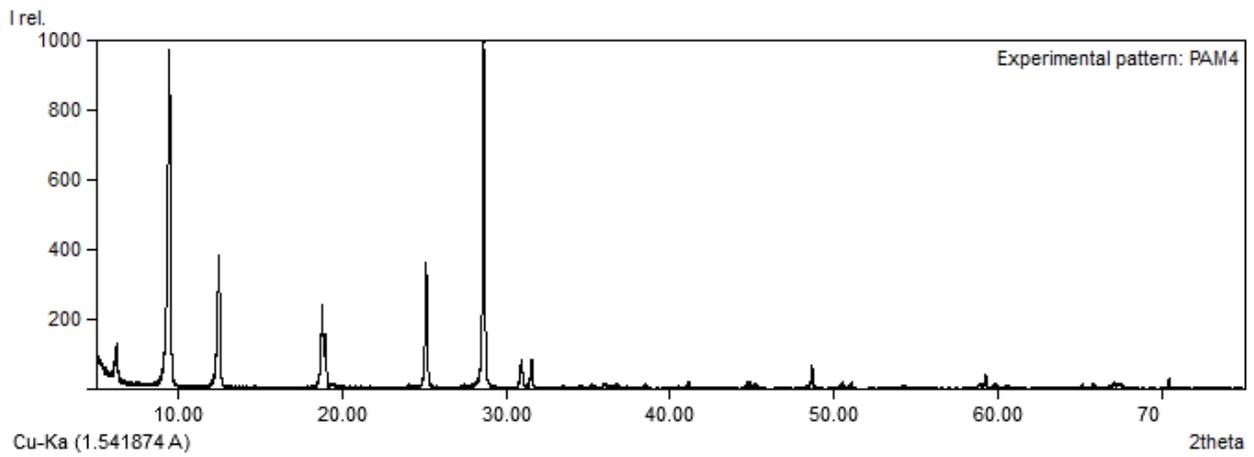


Figure C.h. Sample PAM4.

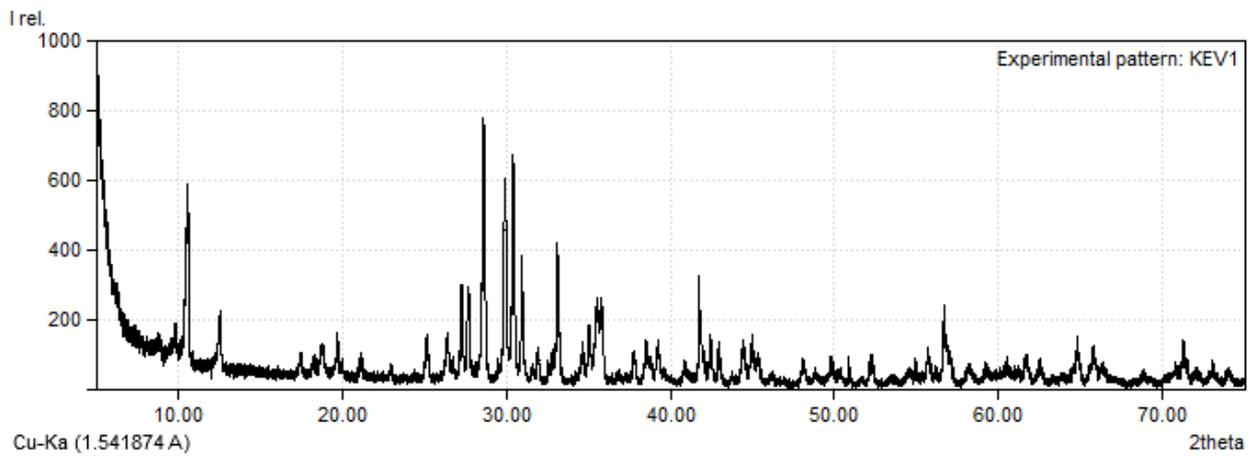


Figure C.i. Sample KEV1.

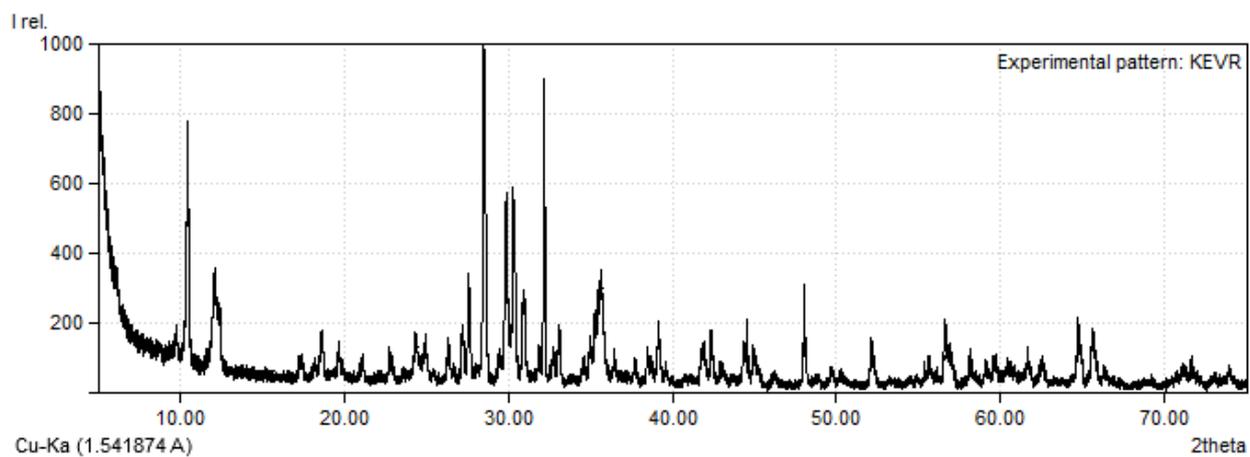


Figure C.j. Sample KEVR.

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