

FINAL REPORT

Mineralogical Investigations of Side and End Products of Mineral Carbonation from the project “CarboResources”

Marshall Plan Scholar Program

by

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During my stay at the University of Pennsylvania I focused on the "Mineralogical Investigations of Side and End Products of Mineral Carbonation". This topic is part of the project "CarboResources" which provides the framework for this research assignment.

This final report is written for the Austrian Marshall Plan Foundation in order to fulfil the Scholarship agreement with Klaus Philipp Sedlazeck.

Introduction

Carbon dioxide is the fifth most abundant gas in the atmosphere and the most important factor for global warming, which provides a lot of motivation for researcher to reduce CO₂ emissions all over the world. Matter et al. (2016) recently published a research paper about the first time permanent disposal of CO₂ as carbonate minerals in basaltic rocks. Adventitiously, mineral waste constituents are the largest waste stream in Europe. As a result, the Montanuniversitaet Leoben initiated the research project "CarboResources" which shall develop a process to carbonate not only mineral waste constituents, but also primary raw materials, to produce filler and construction material for the industry. Hence, this research project focuses on the storage of CO₂ via the carbonation of waste constituents instead of geological formations. All the newly emerging side and end products from this process shall be utilized in various industrial branches.

A successful development will therefore reduce the input of primary raw material for construction purposes, fulfill the waste hierarchy by reducing the amount of waste which is disposed on landfills and will reduce industrial CO₂ emissions. Based on a detailed characterization of primary, but also of secondary raw materials, a multilevel process will be designed and tested with laboratory experiments. On the basis of this, process parameters and reaction conditions can be adapted in order to separate as many side and end products as possible/necessary from the process. Subsequently, these products need to be characterized explicitly and the opportunities for the utilization in various industrial branches have to be identified. All gained results will be included into an energy and mass balance. In addition, a CO₂ balance will be evaluated on a raw material and economic base and a Life Cycle Analysis of the total process will be assessed. This will evince the energy and raw material efficiency of the process to enable a fast realization in the industry.

This research project "CarboResources" is funded by the FFG, Research Studios Austria, and has a duration of 48 month. It is led by the "Chair of Process Engineering" of the Montanuniversitaet Leoben in collaboration with the "Chair of Mining Engineering and Mining Economics" and the "Chair of Waste Processing Technology and Waste Management".

This approach leads to the formation of several targets of this project which shall be answered:

The primary goals of this project are:

- Reduction of industrial CO₂ emissions with simultaneous production of material fractions as cost coverage for the sequestration.
- Characterization and quantification of secondary resources for carbonation and also of primary raw materials.
- Recycling of mineral wastes landfilled today, hence secondary raw materials (e.g. slags and ashes from municipal solid waste incineration plants, residues from salt production).
- Optimization of the carbonation process (dissolving, separation of the side products, carbonation) with special regard to reaction kinetics, yield and purification of the products and recirculation of the additives (e.g. acids).
- Production of Ca- and Mg-carbonates for industrial applications and elaboration of an exploitation strategy.

Secondary goals of this project are:

- Development of a utilization pathway for the emerging side products (e.g. (amorphous) SiO₂, Fe-Oxides and Cr- and Ni-concentrates).
- Establishment of a CO₂ balance and a valuation with regard to raw material economics for the process.

In order to fulfill these goals, emerged side and end products of the carbonation process, but also two primary products from industrial processes were characterized mineralogically in the course of the of the stay abroad.

Detailed presentation of the problem:

The term carbonation is defined as an exothermic reaction of metals with CO₂, leading to the formation of carbonates:



In general, there are two different mechanisms how these carbonates can form, ex-situ and in-situ. In-situ carbonation is the direct reaction of a mineral phase with CO₂, whereas ex-situ or indirect carbonation involves a multistep process such as dissolution and precipitation.

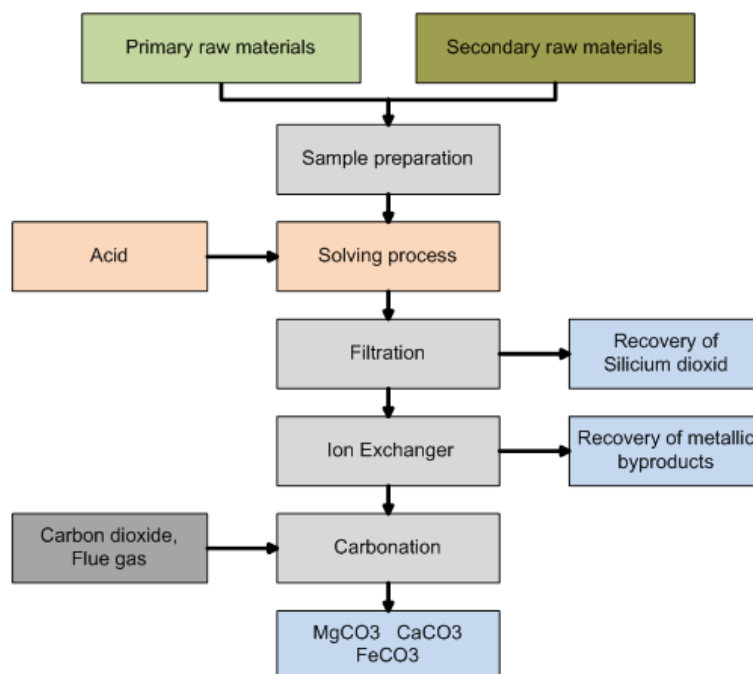


Figure 1: Process overview (Treimer et al. 2014).

Indirect carbonation is technically much more extensive, but also results in much higher efficiency rates. An overview about the indirect carbonation process is schematically shown in Figure 1. Source materials are natural rocks, such as serpentinites, but also Ca- and Mg-rich, alkaline and inorganic industrial residues like slags, e.g. municipal solid waste incineration (MSWI) slags, several ashes, fly ashes and construction wastes.

It can be assumed that the quality of the applied input materials will influence the type and quality of the accruing side and end products, giving rise to the importance of a comprehensive characterization of the input raw materials. These samples are prepared, prior to the dissolving process with acids. Insoluble SiO₂ is segregated and an ion exchanger separates dissolved heavy metals (e.g. Nickel and Chromium), which are then precipitated as oxides. The Ca-, Mg- and Fe-rich water is purged with CO₂ and carbonate phases are forced to precipitate.

As described, three main solid fractions originate during this process. In order to fulfill the waste hierarchy approach (see Figure 2), these three fractions need to be recycled in industrial processes. For this purpose, a detailed characterization of every side and end product is required to be able to ensure the most effective further usage and any negative environmental effects can be excluded. So far, scientists saw the carbonation process as a secure CO₂ storage method, but the feasibility to produce advanced industrial materials has not yet been regarded. Depending on the quality and purity, these produced side and end products can be introduced into industrial processes instead of using primary raw materials.

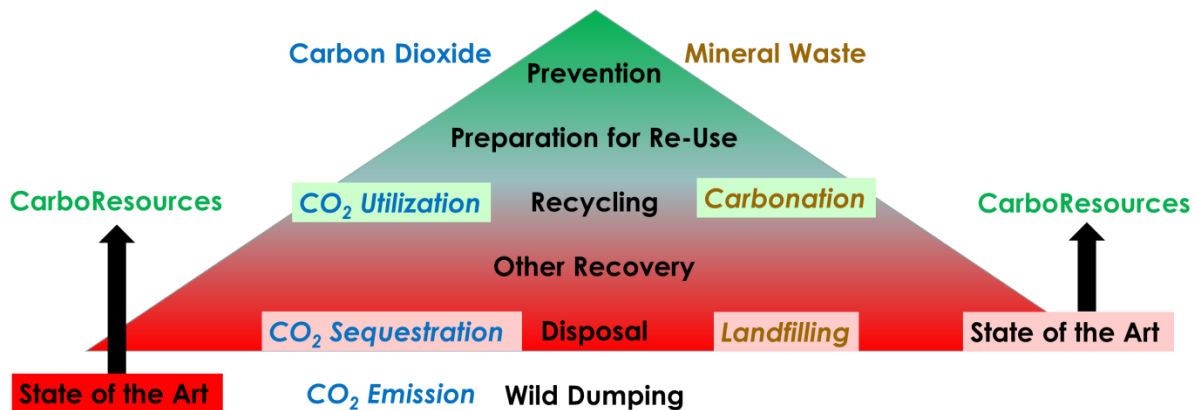


Figure 2: Implication of the project "CarboResources" to the waste hierarchy (after: Höllen et al. 2015).

From a waste management point of view, the project can improve the state of the art in two different ways. Even though, the waste hierarchy (Figure 2) is usually adduced for solid wastes (Mineral waste, right side), in this case, it can also be projected to carbon dioxide (left side). The emission of CO₂ into the atmosphere is currently state of the art and can be compared to the wild dumping of waste; the sequestration of CO₂ is momentarily in the focus of many researchers, controversy debated and corresponds to the landfilling of waste. For mineral wastes, the disposal on landfills is the state of the art and no further use is applied. The project CarboResources will utilize CO₂ by the carbonation of mineral waste, yielding to an improvement of the state of the art on both sites of the waste hierarchy.

Up to now, the primary and secondary raw materials have been identified, quantified and characterized. First dissolving experiments have been conducted in the laboratory.

Prior to the stay at the University of Pennsylvania, the project leader passed emerged products from the dissolution process, but also some of the introduced primary products of some of the experiments for the mineralogical characterization. Unfortunately, the first carbonation experiments were not yet completed by this time. A detailed mineralogical investigation of the samples is the task of the "Chair of Waste Processing Technology and Waste Management" at the University of Pennsylvania. In this step, it is very important to

identify potential impurities which influence the overall process. A comparison between the side and end products, emerging from primary and secondary raw materials was performed.

Materials and Methods

As already mentioned before, the "Chair of Waste Processing Technology and Waste Management" is in charge of the mineralogical characterization of the residues, the metal concentrates and also would have been in charge of the examination of the carbonates as well, but the carbonates were not ready yet by the date of the approach. Depending on the input material, these products may vary and it is important to investigate these differences to be able to give an accurate prediction about the expected end products which shall be utilized in various industrial branches.

Mineral waste constituents, such as MSWI slags, add up to the largest waste stream in Europe, hence is in the primary focus of this study.

During the stay at the University of Pennsylvania, research was conducted with natural primary raw material, a serpentinite from the quarry Preg, close to Graz, Styria, Austria and a dust from the steel plant "Böhler" as well as residues from the dissolving processes of these raw materials. As mentioned before, the precipitated carbonates and metal concentrates could not have been analyzed during this stay.

Table 1: Sample overview and description.

Sample ID	Material	Properties	Experiment Conditions
19	Serpentinite	63 - 125 µm	-
285	Dust "Böhler"	63 - 125 µm	-
239	Serpentinite (19)	50 g / 600 ml HCL (8 %)	80 °C / rpm = min for 3 h
292	Serpentinite (19)	50 g / 600 ml HCL (19 %)	80 °C / rpm = max for 3 h
298	Serpentinite (19)	50 g / 600 ml HCL (19 %)	80 °C / rpm = max for 3 h
316	Serpentinite (19)	50 g / 800 ml HCL (19 %)	80 °C / rpm = max for 3 h
289	Dust "Böhler" (285)	50 g / 600 ml HCL (8 %)	80 °C / rpm = min for 3 h
319	Dust "Böhler" (285)	50 g / 600 ml HCL (8 %)	80 °C / rpm = min for 3 h
322	Dust "Böhler" (285)	50 g / 600 ml HCL (8 %)	80 °C / rpm = min for 3 h
352	Serpentinite (19)	16.67 g / 200 ml HCL (8 %)	80 °C / rpm = min for 3 h + Ultrasound
355	Serpentinite (19)	16.67 g / 200 ml HCL (8 %)	80 °C / rpm = min for 3 h + Ultrasound
358	Serpentinite (19)	16.67 g / 200 ml HCL (8 %)	80 °C / rpm = min for 3 h + Ultrasound

In total, there were 12 different samples forwarded from the project leader, "Chair of Process Engineering" of the Montanuniversitaet Leoben. Two samples were the original raw

material samples and the other 10 samples consisted of the residue after cooking the original raw material in HCL. A detailed sample description is provided in Table 1. The original material, used for the experiments, had a grainsize between 63 - 125 µm.

The other samples result from cooking the powder in a beaker at 80 °C for 3 hours but some boundary conditions varied. During this cooking process, the material was stirred and for some samples, an ultrasound was additionally applied. Experiments were performed with different HCl concentrations, volumes as well as sample masses. These different properties and experimental set ups should deliver information about the optimum dissolving conditions.

Due to the extremely fine grain size which was used for the experiments, resulting sample grain size set up limits for microscopic analyses. For the transmitted light microscopy, as well as for electronic microscopy, a sand back surface of the mineral grains is required. In order to establish this, they need to be embedded into an epoxy resin. This was not possible because the adhesive ability of the epoxy resin is not sufficient enough to embed such a small grain size fraction. The required force for polishing the sample would have dislanted the mineral grains.

According to the research proposal, it was anticipated to perform the mineralogical characterization by using a direct solid atomic absorption spectrometer. However, this newly purchased machine was not ready to be used yet due to diverse technical problems. Anticipated analyses were alternatively performed by ICP-OES analyses. Additionally, Powder X-ray diffraction (XRD) and x-ray fluorescence spectroscopy (XRF) were carried out at the Department of Earth and Environmental Science of the University of Pennsylvania.

XRD data were collected with a *Panalytical X'Pert Powder X-Ray Diffractometer*. According to the available sample mass, two different sample holders were used. In some samples, mineral grains stuck together. In this case, the samples were ground in a mortar, prior to placing them into the sample holder. XRD datasets were collected in a 2θ angle range between 5° and 70° and an increment of 0.0170° and a scan step time of 59.69 s. Additionally, the sample was rotated during the measurement to prevent a preferred orientation of the crystals.

A semi quantitative chemical bulk rock analysis was acquired by using a *Panalytical Epsilon-1 Benchtop X-Ray Fluorescence Spectrometer* by placing the untreated, forwarded sample into the sample holder cups. The samples were analyzed by using the implemented standard Panalytical measuring program.

For the quantitative analysis, sample preparation was more sophisticating. The *Spectro Genesis ICP-OES*, used for the analysis, required samples in liquid state, hence, a microwave digestion was performed. Microwave digestion was done according to the EPA Method 3052. An acidic mixture of 9 mL of Nitric acid, 5 mL of HF and 2 mL of HCl was mixed with 1 g of

sample material in an inert polymeric microwave vessel. The temperature profile is specified to permit specific reactions and incorporates reaching 180 ± 5 °C in approximately less than 5.5 minutes and remaining at 180 ± 5 °C for 9.5 minutes for the completion of specific reactions. The ICP-OES system is strongly sensitive to HF, therefore the samples were diluted to a HF concentration of 1 % prior to the introduction into the system. Samples 322, 319 and 289 were completely digested, but during the cooling of the samples and the dilution, a green precipitate formed, so the samples had to be digested and measured again. The second measuring was done at the laboratory of the Chair of Waste Processing Technology and Waste Management of the Montanuniversitaet Leoben. According to the project leader, elements of interest were Mg, Si, Ca, Mn, Ni, Fe and Cr.

Results and Discussion

As described in the Materials chapter, the samples consist of different sample materials, a naturally occurring serpentinite and a dust from a steel plant as well as the resulting residues from the dissolving process in HCl. In the following, analytical results of all samples will be presented together, but discussed in groups of the specific applied raw material and their originating samples from the dissolving experiments.

XRD Analyses

Acquired XRD patterns from samples 19 and 285 are exemplarily displayed in Figure 3 and Figure 4. The other patterns are to find in Figure 5 to Figure 14 in the appendix. A clear summary of these XRD-analyses results is provided in Table 2. Identified mineral phases in the samples are: antigorite ($(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$), clinochrysotile ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), lizardite ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), forsterite (Mg_2SiO_4), riebeckite ($\text{Na}_2(\text{Fe,Mg})_3\text{Fe}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$), tremolite ($\text{Ca}_2\text{Mg}_5(\text{Si}_8\text{O}_{22})(\text{OH})_2$), chlinochlore ($(\text{Mg,Fe})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$), hedenbergite ($\text{CaFeSi}_2\text{O}_6$), omphacite ($(\text{Ca,Na})(\text{Mg,Fe}^{2+},\text{Fe}^{3+},\text{Al})\text{Si}_2\text{O}_6$), diopside ($\text{CaMgSi}_2\text{O}_6$), vermiculite ($\text{Mg}(\text{Mg,Fe,Al})_6(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot 8\text{H}_2\text{O}$), mullite ($\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ $\{x \approx 0.4\}$), quartz (SiO_2), hematite (Fe_2O_3), eskolaite (Cr_2O_3), magnetite (Fe_3O_4), donathite (FeCr_2O_4), magnesioferrite (MgFe_2O_4), powellite (CaMoO_4), periclase (MgO), portlandite ($\text{Ca}(\text{OH})_2$), calcite (CaCO_3), larnakite ($\text{Pb}_2(\text{SO}_4)\text{O}$), sphalerite ($(\text{Zn,Fe})\text{S}$), mawsonite ($\text{Cu}_6\text{Fe}_2\text{SnS}_8$) and fluorite (CaF_2).

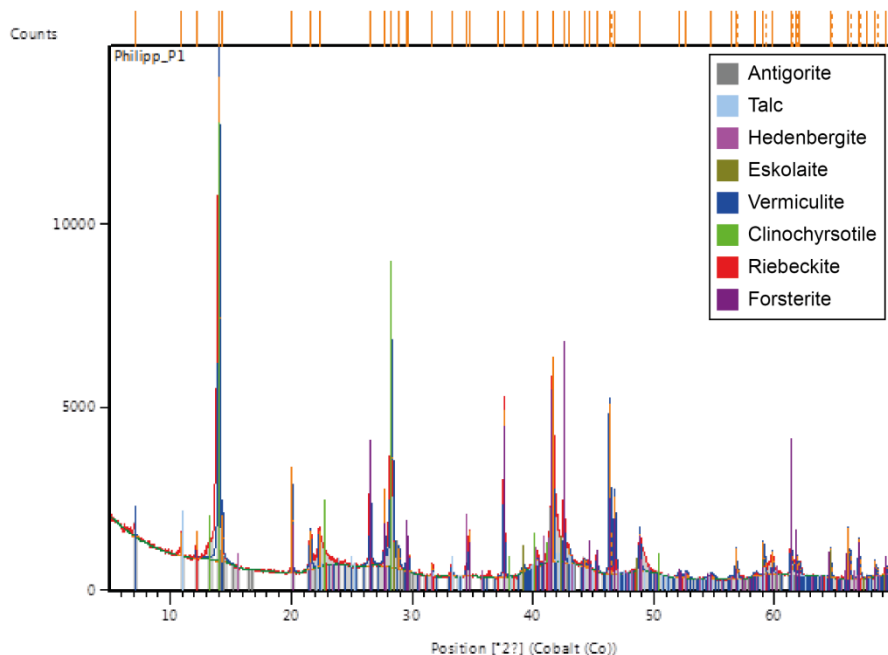


Figure 3: XRD pattern of sample 19.

In sample 19 (Figure 3), the two serpentine group members antigorite and clinochrysotile, the orthopyroxene hedenbergite, the Cr-oxide eskolaite of the hematite group, the clay mineral vermiculite, the sheet silicate talc, the Mg end-member of the olivine family forsterite as well as the amphibole riebeckite were proven. All these solid phases are minerals that typically occur in ultramafic rocks, hence are common in serpentinites, such as the first raw material, from sample 19.

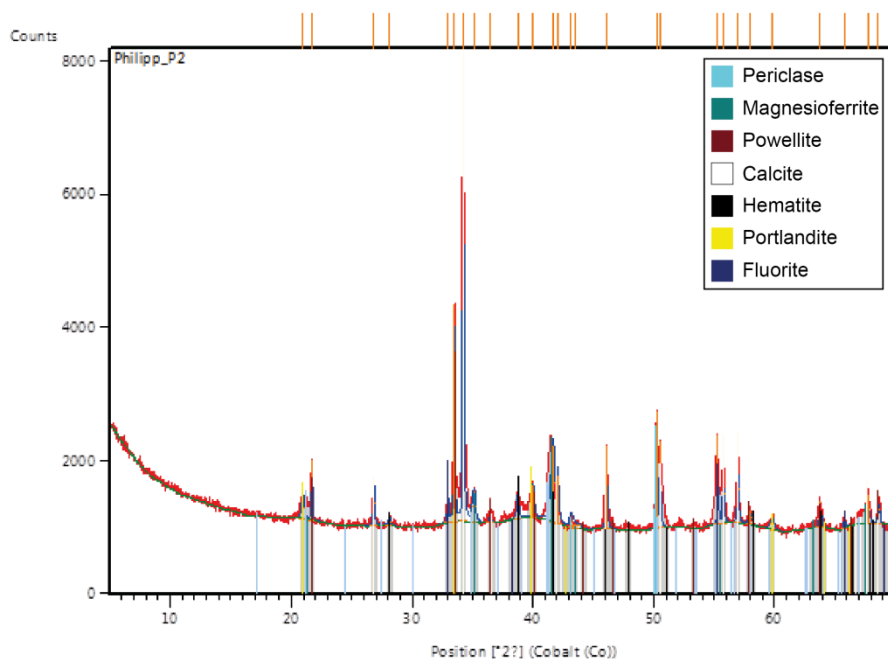


Figure 4: XRD pattern of sample 285.

The second raw material, sample 285 (Figure 4), a dust from a steel plant, consists of the mineral phases periclase, magnesioferrite, powellite, calcite, hematite, portlandite and fluorite, hence totally different mineral types compared to sample 19. All the identified minerals are either (mon-)oxides, hydroxides, carbonates or fluorites. Magnesioferrite and powellite are spinel type oxides, whereas hematite belongs to the corundum group. Periclase is a Mg-monoxide. Ca bearing minerals are the Ca-carbonate calcite, Ca-hydroxide portlandite as well as the Ca-halogenite fluorite.

The following samples result from cocking sample 19 in HCl, according to the experiment properties, listed in Table 1. Samples 298 (Figure 6) and 292 (Figure 7) are directly comparable, whereas the experimental parameters of samples 239 (Figure 5) and 316 (Figure 8) are slightly different. Sample 239 was produced by using a lower concentrated HCl and for the production of sample 316, a higher acid volume was chosen in order to gain an idea about the effects of the parameter changes. Samples 352, 355 and 358 can be

compared to each other. Additionally, the effect of an ultrasound during the cooking process can be studied.

If a mineral phase was present in the samples of the raw material, but is not present in the resulting sample from the dissolving process, this either means that this phase dissolved or it was not present in the material which was used for the experiment due to heterogeneity. The fact that a very small grain size was used for the experiments minimizes the probability of a lack of phases. Vice versa, if a phase is present in the products of the experiments, but not in the educts, this means that the phase precipitated during the experiment or was not present in the introduced material.

Antigorite is present in sample 19 and also in all the samples (residues from dissolving the serpentinites) but 239 and 292. The experimental setup suggests that the resulting sample 239 and 292 rather do not have the most aggressive dissolving power, hence it seems that the dissolution process has none or only a minor effect on the dissolution of antigorite. An effect of the ultrasound on the solubility of antigorite was not proven.

However, it seems like the ultrasound has an effect on the dissolution of clinochrysotile, because no clinochrysotile was present in samples 239, 298, 292 and 316, but not in 352, 355 and 358. Lizardite was not present in the raw material, though it was detected in samples 298, 292 and 316. The conditions during the experiment must have favored a precipitation of lizardite. A phase transition from the polymorph clinochrysotile could also be an explanation.

Talc was found in all samples, yielding to the assumption that the acid has no effect on the dissolution of the talc; the same accounts for the amphibole riebeckite and the clay mineral vermiculite.

An overall positive effect of the acid on the dissolution of forsterite was not proven because it was still present in some of samples. Anyhow, a positive effect of the ultrasound could be assumed because no forsterite was found in the ultrasound samples. The abundance of chlinochlore solely in the ultrasound samples leads to the assumption that the ultrasound helps to form chlinochlore from solution. The same almost accounts for tremolite, but this mineral phase is also present in sample 316, where a higher volume of acid was used. It seems like tremolite favors a higher acidity.

Hedenbergite seems to dissolve in the acid bath, even though it was still detected in sample 298. A clear relationship about the dissolution or precipitation of omphacite cannot be made; however, omphacite was present only in samples 292 and 316. These two experiments do not have the same setup which makes it impossible to give an assumption about the stability of the mineral phase.

The presence of the Cr-oxide eskolaite in the raw material, but in none of the products clearly shows that eskolaite dissolves due to acidic conditions.

Table 2: Summary XRD Analyses.

Mineral	Chemical Formula	Sample											
		19	285	239	298	292	316	352	355	358	322	319	289
Antigorite	(Mg,Fe) ₃ Si ₂ O ₅ (OH) ₄	X	-	-	X	-	X	X	X	X	-	-	-
Clinochrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	X	-	X	X	X	X	-	-	-	-	-	-
Lizardite	Mg ₃ Si ₂ O ₅ (OH) ₄	-	-	-	X	X	X	-	-	-	-	-	-
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	X	-	X	X	X	X	X	X	X	-	-	-
Forsterite	Mg ₂ SiO ₄	X	-	X	-	X	X	-	-	-	-	-	-
Riebeckite	Na ₂ (Fe,Mg) ₃ Fe ₂ Si ₈ O ₂₂ (OH) ₂	X	-	X	X	X	X	X	X	X	-	-	-
Tremolite	Ca ₂ Mg ₅ (Si ₈ O ₂₂)(OH) ₂	-	-	-	-	-	X	X	X	X	-	-	-
Chlinochlore	(Mg,Fe) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	-	-	-	-	-	-	X	X	X	-	-	-
Hedenbergite	CaFeSi ₂ O ₆	X	-	-	X	-	-	-	-	-	-	-	-
Omphacite	(Ca,Na)(Mg,Fe ²⁺ ,Fe ³⁺ ,Al)Si ₂ O ₆	-	-	-	-	X	X	-	-	-	-	-	-
Diopside	CaMgSi ₂ O ₆	-	-	-	-	-	-	-	-	-	-	-	X
Vermiculite	Mg(Mg,Fe,Al) ₆ (Si,Al) ₈ O ₂₀ (OH) ₄ ·8H ₂ O	X	-	X	X	X	X	X	X	X	-	-	-
Mullite	Al _{4+2x} Si _{2-2x} O _{10-x} {x ≈ 0.4}	-	-	-	-	-	-	-	-	-	X	X	-
Quartz	SiO ₂	-	-	-	-	-	-	-	-	-	X	X	-
Hematite	Fe ₂ O ₃	-	X	-	-	-	-	-	-	-	X	X	X
Eskolaite	Cr ₂ O ₃	X	-	-	-	-	-	-	-	-	-	-	-
Magnetite	Fe ₃ O ₄	-	-	-	-	-	-	-	-	-	X	X	-
Donathite	FeCr ₂ O ₄	-	-	-	-	-	-	-	-	-	X	X	-
Magnesioferrite	MgFe ₂ O ₄	-	X	-	-	-	-	-	-	-	-	-	X
Powellite	CaMoO ₄	-	X	-	-	-	-	-	-	-	-	-	-
Periclase	MgO	-	X	-	-	-	-	-	-	-	-	-	-
Portlandite	Ca(OH) ₂	-	X	-	-	-	-	-	-	-	-	-	-
Calcite	CaCO ₃	-	X	-	-	-	-	-	-	-	-	-	-
Larnakite	Pb ₂ (SO ₄)O	-	-	-	-	-	-	-	-	-	-	-	X

Table 2 continued

Sphalerite	(Zn,Fe)S	-	-	-	-	-	-	-	-	-	-	X	X	-
Mawsonite	Cu ₆ Fe ₂ SnS ₈	-	-	-	-	-	-	-	-	-	-	X	X	-
Fluorite	CaF ₂	-	X	-	-	-	-	-	-	-	-	X	X	X

The XRD results of the dust from the steel plant and resulting cocking products clearly show that the mineral phases hematite and fluorite reveal unchanged during the cocking process in acid because they are present in all samples.

Powellite, periclase, portlandite and calcite were dissolved during the boiling in HCl. They were detected in the raw material, but not in the residues.

By comparing the mineral phases diopside, mullite, quartz magnetite, donathite, larnakite, sphalerite and mawsonite, sample 289 behaved different to samples 322 and 319. None of these phases was present in the raw material. The orthopyroxene diopside as well as the lead sulphate larnakite were present in sample 289, but in no other sample, whereas mullite, quartz, magnetite, sphalerite and mawsonite were found in 322 and 319, but not in the others.

Even though it was not detected in sample 285, quartz was probably also present in the raw material. In samples 322 and 319 quartz was found but no SiO₂ bearing species, which dissolved during the cocking process, was identified in sample 285.

Magnesioferrite was identified in sample 289 and also in the raw material.

High intensities in the XRD patterns in the form of a bump-shape at low 2 θ ranges reveal high amounts of amorphous material.

XRF Analyses

The semi quantitative XRF analysis was performed for several reasons. One reason was to gain an idea about a concentration range of the abundance of the elements of interest. A second reason was to acquire information about the appearance of elements which are not directly in the focus of attention, but still occur in quite high amounts such as Mo. The third reason is the analysis of Si. The analysis of Si is well known to be difficult via ICP-OES. XRF delivers semi quantitative, but it is sufficient enough for Si investigations. Table 3 shows the results of the XRF measurements. In this chapter, only the analysis of the elements, which were not measured quantitatively with the ICP-OES as described.

The passive enrichment of SiO₂ due to dissolution of the less stable phases is clearly proven by the XRF analysis. All samples show enrichment factors from 2 to 7. Especially the residues from the dust samples from the steel factory show high enrichment rates of SiO₂.

Al concentration reveal an enrichment factor of about 2 in most the residues of serpentinite. The Al concentrations in the residues are around 1 %. According to the XRD analyses, Al is present as vermiculite and clinocllore. Al abundance slightly increases in residues due to the cocking process.

The measured Zn concentrations confirm the XRD results. Sphalerite, the Zn-sulfide mineral phase was detected in samples 322 and 319. These samples also show higher Zn concentrations in the XRF measurement. Zn was also encountered in samples 289 and the original dust, but the concentration was probably not sufficient enough to be detected via XRD or the Zn phase was present as an amorphous phase.

The Mo concentration decreases with coking which means that the Mo bearing phase dissolves during the process which is also shown by the XRD analysis because the only identified Mo bearing phase is powellite and it was present in the raw material sample 285.

Table 3: XRF Analyses.

Compound	Unit	sample 19	285	239	298	292	316	289	319	322	352	355	358
Na ₂ O	%	-	-	-	3.84	-	-	-	-	-	-	-	-
MgO	%	34.787	8.282	7.355	6.154	7.489	6.33	1.516	1.328	1.631	4.951	5.61	5.068
Al ₂ O ₃	%	0.433	0.738	1.029	-	1.019	1.01	0.997	0.913	0.898	1.348	1.549	1.327
SiO ₂	%	27.786	2.994	63.417	59.508	67.628	67.947	19.534	22.141	22.195	62.014	64.637	67.591
P ₂ O ₅	%	0.339	0.151	0.379	0.369	0.38	0.377	0.235	0.25	0.243	0.403	0.394	0.403
SO ₃	%	0.111	0.304	0.108	0.08129	-	-	0.05967	-	-	0.139	0.127	0.132
Cl	%	0.115	0.271	0.09299	3.699	0.09329	0.254	0.301	0.412	0.79	0.154	0.109	0.104
K ₂ O	%	0.00885	0.654	0.00644	0.00729	0.00912	0.00763	0.07428	0.06776	0.07447	0.00846	0.00819	0.00897
CaO	%	0.407	40.106	0.263	0.263	0.368	0.308	4.319	3.133	3.207	0.229	0.194	0.31
V ₂ O ₅	%	-	0.996	0.0029	0.00359	0.00415	0.00365	0.303	0.286	0.272	0.00402	0.00414	0.00441
Cr ₂ O ₃	%	0.242	6.622	0.333	0.305	0.453	0.36	20.074	21.318	20.436	0.331	0.352	0.384
MnO	%	0.105	4.508	0.01892	0.01657	0.02601	0.01668	2.685	2.8	2.708	0.00682	0.00623	0.00895
Fe ₂ O ₃	%	8.422	15.07	1.7	1.197	2.111	1.219	28.887	27.115	26.915	0.425	0.397	0.499
CuO	%	-	0.172	-	-	-	-	0.271	0.29	0.277	-	-	-
ZnO	%	0.00479	0.934	0.00167	0.00162	0.00328	0.00221	1.023	1.056	1.054	0.00073	0.00062	0.00016
MoO ₃	%	-	4.635	-	-	0.0037	0.00204	1.628	1.983	2.317	-	-	-
Yb ₂ O ₃	%	-	0.217	-	-	-	-	0.443	0.576	0.654	-	-	-
TiO ₂	ppm	79.9	436.1	54.9	42.6	68.8	55.1	1100	1130	1130	83	63.4	81.4
NiO	ppm	3880	8310	818.9	648.7	989.2	589.2	21960	23060	22710	289.4	295.6	308.1
GeO ₂	ppm	-	-	-	-	-	-	-	-	274.1	-	-	-
As ₂ O ₃	ppm	-	-	-	-	-	-	-	-	7.3	-	-	-
SeO ₂	ppm	-	79.6	-	-	-	-	175.9	219.1	211.6	-	-	-
Rb ₂ O	ppm	1.3	32.4	-	-	-	-	23	23.2	23	-	-	-
SrO	ppm	-	135.3	-	-	-	-	8.9	-	-	-	-	-

Table 3 continued

Y ₂ O ₃	ppm	-	5	-	-	-	-	-	2.2	4.2	-	-	-
ZrO ₂	ppm	-	76.5	-	-	-	-	156.4	139.1	133.3	-	-	-
Nb ₂ O ₅	ppm	-	432.9	-	-	-	-	1070	1060	1080	-	-	-
SnO ₂	ppm	69.6	107.9	41.9	-	40.9	38.3	-	-	88.3	33.4	35.3	36.6
TeO ₂	ppm	-	-	-	-	24	-	-	-	-	-	-	-
Br	ppm	-	-	-	4.5	-	-	-	-	-	-	-	-
La ₂ O ₃	ppm	37.3	-	4	2.1	3	-	-	-	-	-	-	-
OsO ₄	ppm	-	-	-	-	-	-	-	-	-	-	-	-
HgO	ppm	-	171.2	-	-	-	-	328.2	438.5	280.1	-	-	-
PbO	ppm	-	315.1	-	-	-	-	213.1	235.1	207.6	-	-	-
Bi ₂ O ₃	ppm	-	-	-	-	-	-	-	18.9	-	-	-	-
Pr ₂ O ₃	ppm	-	-	-	1.1	-	-	-	-	-	-	-	-
Re	ppm	4.1	-	3.1	2	2	2.9	-	-	-	3.2	2.1	2.4

In the dust samples, concentrations of Ti, Zr and Nb are generally relatively low but doubled during the cocking process. Especially Ti and Zr tend to form very resistant oxides and silicates. However, it was found that the Ti concentrations in the serpentinite samples tend to decrease through the cocking process.

All these results have to be seen with caution because they were obtained with a non-standardized method; however, they provide a rough estimation about the element concentrations and distributions in the samples.

ICP-OES Analyses

ICP-OES analyses were carried out to quantify the concentration changes of the elements of interest. Measured concentrations of the ICP-OES are listed in Table 4 as well as the detection limit. Resulting solid concentrations are compiled in Table 5. Due to the precipitation of solids from solution, samples 289, 319 and 322 had to be measured again as described. Presented concentrations in Table 5 are the remeasured concentrations.

Table 4: Measured concentrations in dilution via ICP-OES analyses. Samples, marked with a * were remeasured in laboratory of the Chair of Waste Processing Technology and Waste Management of the Montanuniversitaet Leoben. Presented measurements here were neglected.

Sample	Ca mg/l	Fe mg/l	Cr mg/l	Mg mg/l	Mn mg/l	Ni mg/l
Blank	< -0.004	< -0.202	< 0.002	< -0.030	< -0.188	<-0.065
19	4.839	12.728	0.617	1.301	2.709	9.391
285	6.096	86.787	74.246	0.513	47.176	42.642
239	10.938	7.822	2.618	5.949	1.27	3.124
298	9.466	5.372	1.866	5.423	0.525	2.245
292	10.424	8.5	3.179	4.221	0.633	2.778
316	11.222	7.23	4.377	7.689	0.35	2.098
352	12.297	2.438	3.906	11.471	< -0.016	0.79
355	10.729	3.278	4.976	9.73	< 0.001	0.777
358	10.794	2.9	3.943	12.273	< -0.001	0.847
322*	3.934	137.429	66.488	0.177	21.498	40.739
319*	4.226	139.491	76.758	0.114	22.637	43.244
289*	4.402	134.801	76.951	0.095	20.456	48.565

Evaluation of this data revealed that the obtained data for sample 19 cannot be correct. Magnesium concentrations are too low for a serpentinite. The samples are turned in into the laboratory of the Chair of Waste Processing Technology and Waste Management of the Montanuniversitaet Leoben for remeasuring, but by the time of finishing this report, the results were not obtained yet.

Anyhow, by comparing the semi quantitative results from sample 285 from the XRF analysis to the results, obtained from the ICP analysis from samples 322, 319 and 289 several changes are obvious.

The original dust mostly consists of Ca, Fe, Mg, Cr and Mn, whereas the residues indicate increased contents of Fe, Cr, Mn and Ni. Mg and Ca bearing phases must have dissolved leading to a decreasing content in the residues. Concentrations of Si also increase from around 3 % to around 20 %. This increase in heavy metal content makes a further utilization of the products very difficult due to restraints by the government.

Table 5: Calculated concentration in solid samples. Samples, marked with a * are the remeasured samples from the laboratory of the Chair of Waste Processing Technology and Waste Management of the Montanuniversitaet Leoben.

Sample	Ca mg/kg TS	Fe mg/kg TS	Cr mg/kg TS	Mg mg/kg TS	Mn mg/kg TS	Ni mg/kg TS
19	1,202	3,163	153	323	673	2,333
285	1,516	21,586	1,8467	128	1,1734	10,606
239	2,718	1,944	651	1,478	316	776
298	2,354	1,336	464	1,349	131	558
292	2,595	2,116	791	1,051	158	692
316	2,791	1,798	1,089	1,912	87	522
352	2,975	590	945	2,776	-	191
355	2,671	816	1,239	2,422	-	193
358	2,685	721	981	3,053	-	211
322*	19,700	200,000	120,000	3,760	9,500	23,600
319*	23,400	240,000	150,000	3,900	8,760	25,000
289*	24,400	240,000	150,000	3,580	8,950	29,800

By the time of the final evaluation of this data, the results from the lab were not obtained yet. If a completion of the results is requested by the Marshall Plan Scholar Program, the results can subsequently be added to this report. However, the results will soon be implemented into a paper which then is tried to be published in a peer reviewed journal.

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Appendix

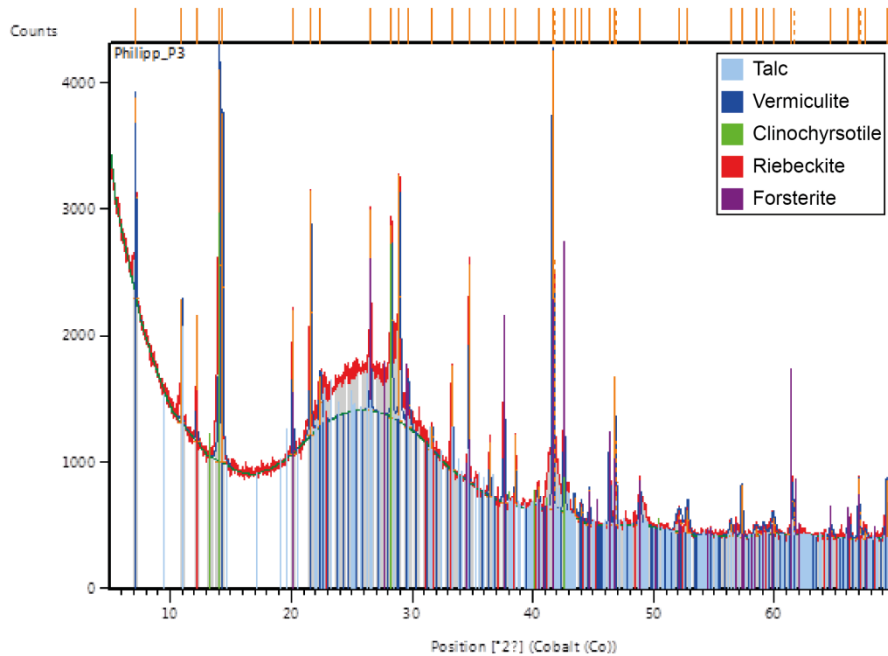


Figure 5: XRD pattern of sample 239.

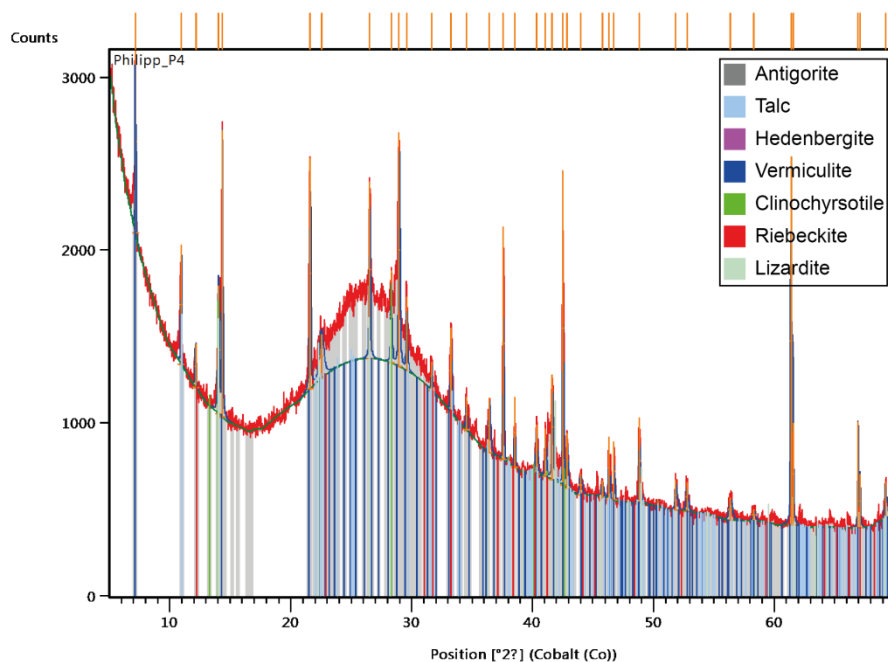


Figure 6: XRD pattern of sample 298.

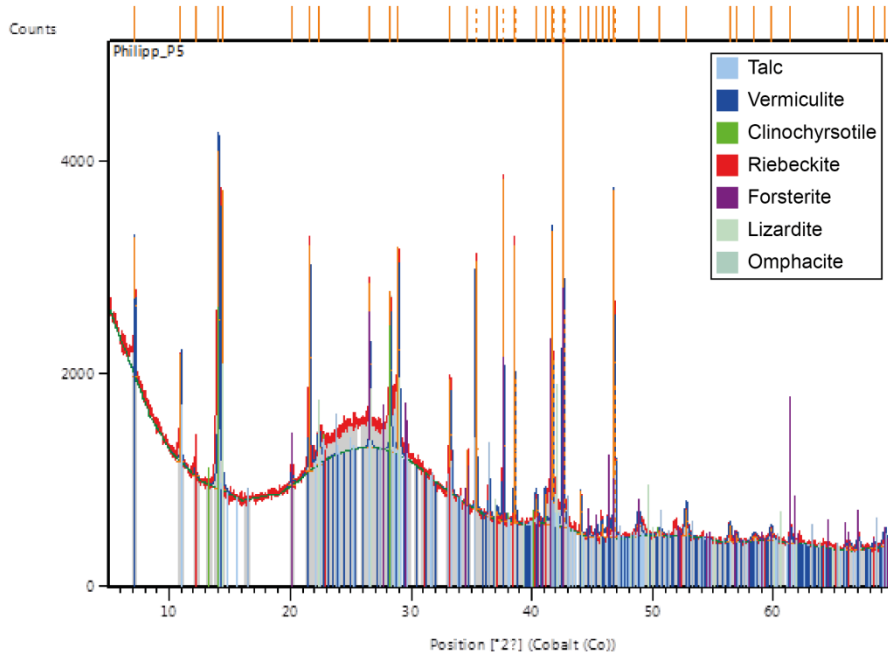


Figure 7: XRD pattern of sample 292.

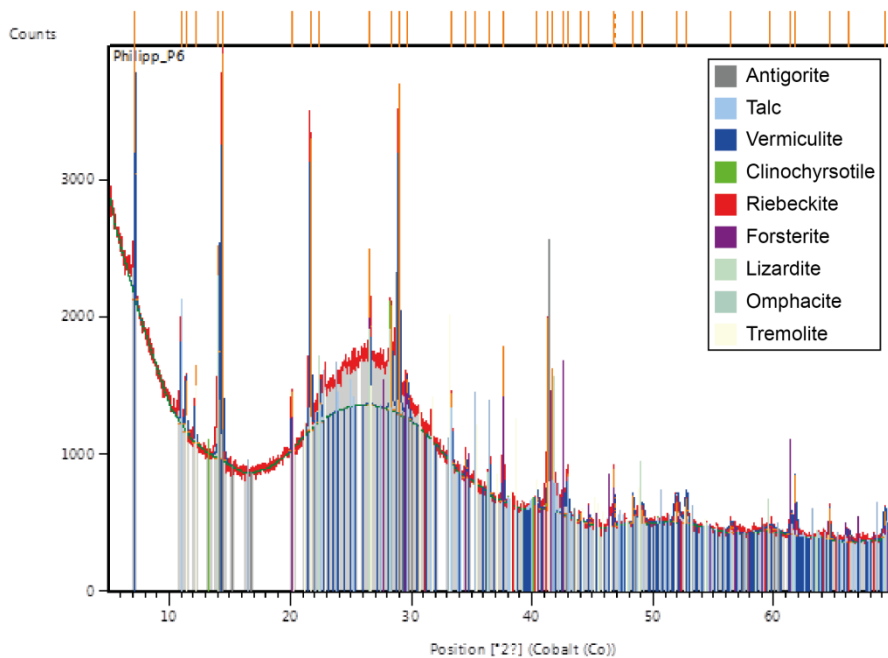


Figure 8: XRD pattern of sample 316.

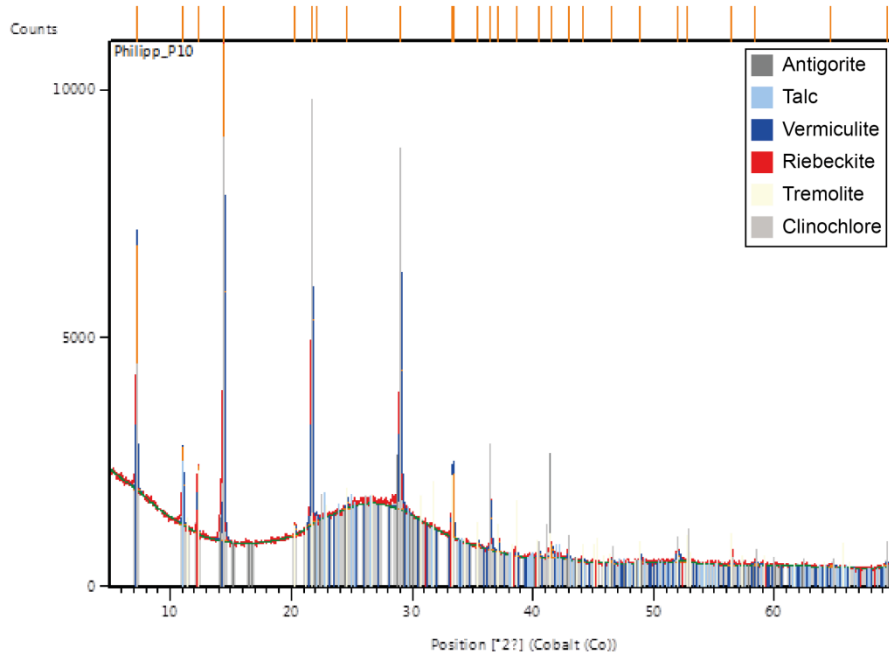


Figure 9: XRD pattern of sample 352.

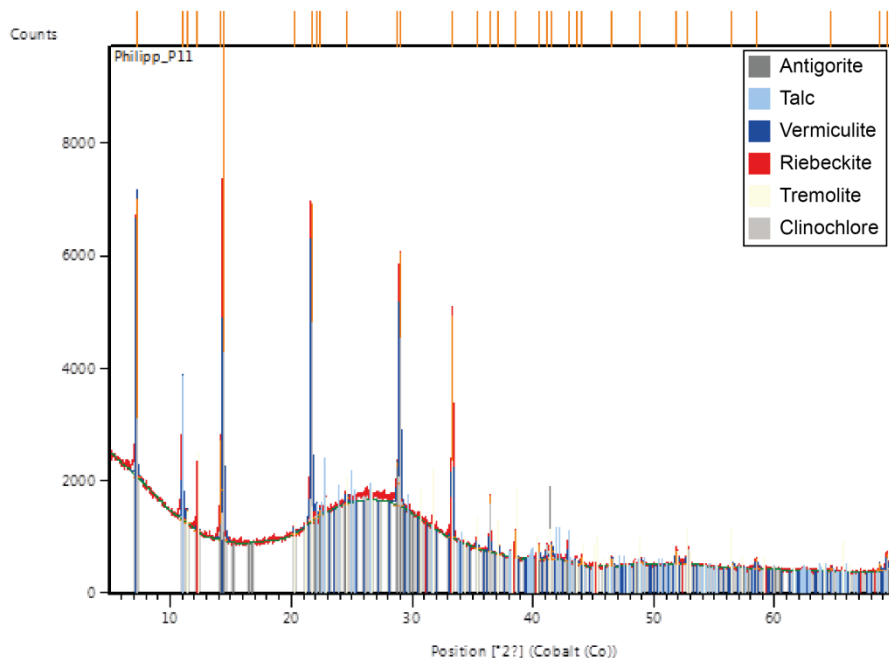


Figure 10: XRD pattern of sample 355.

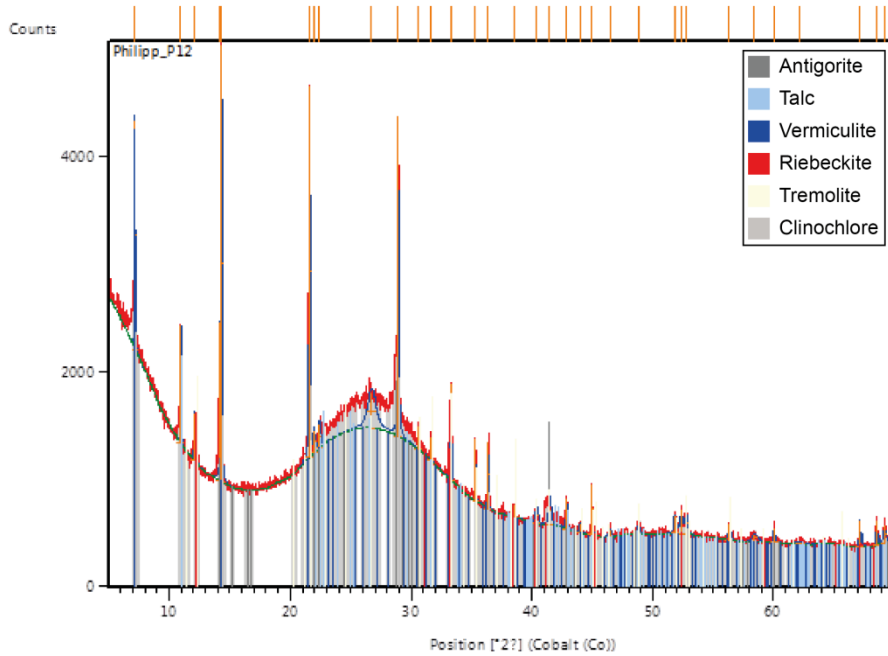


Figure 11: XRD pattern of sample 358.

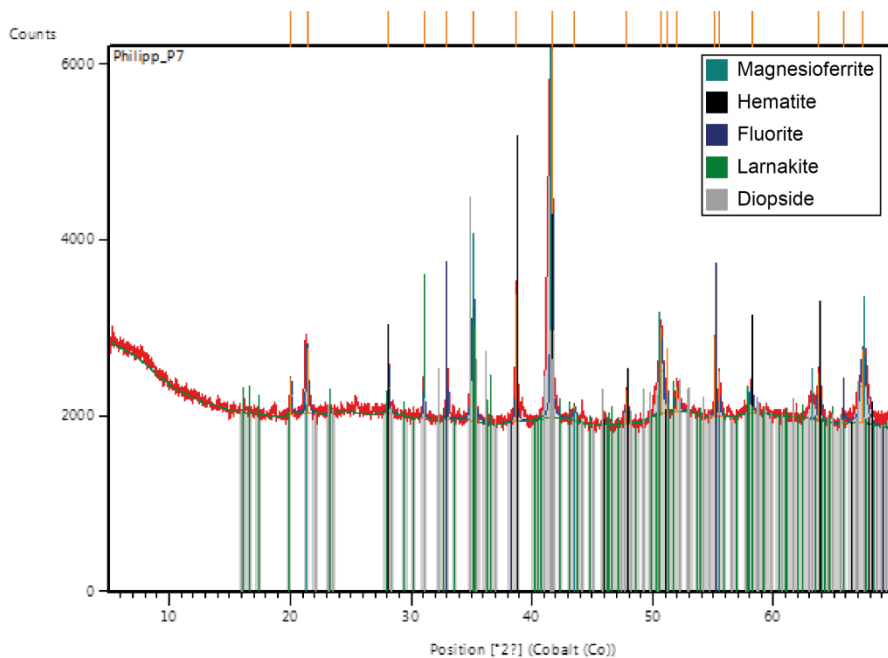


Figure 12: XRD pattern of sample 289.

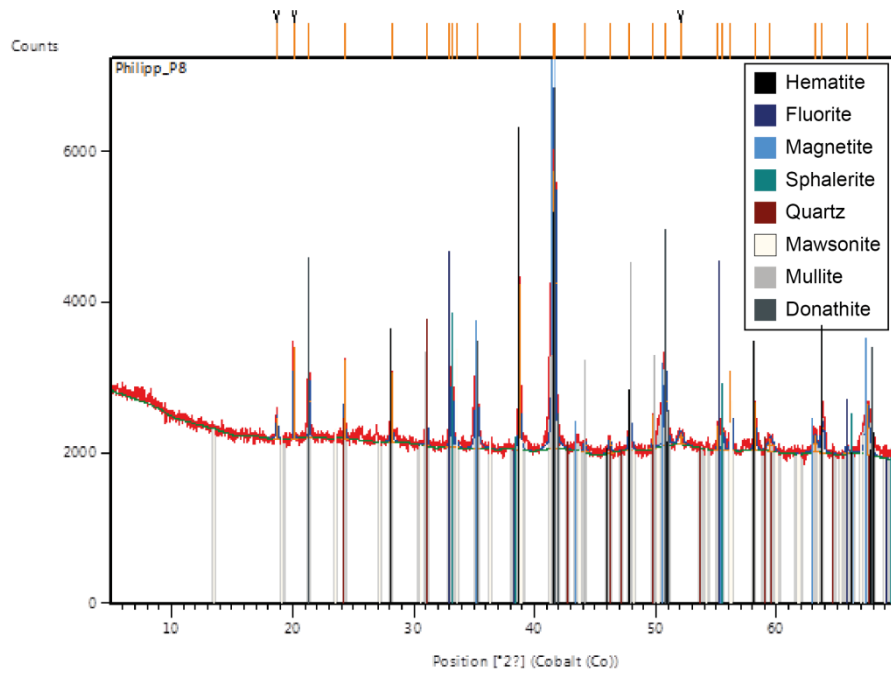


Figure 13: XRD pattern of sample 319.

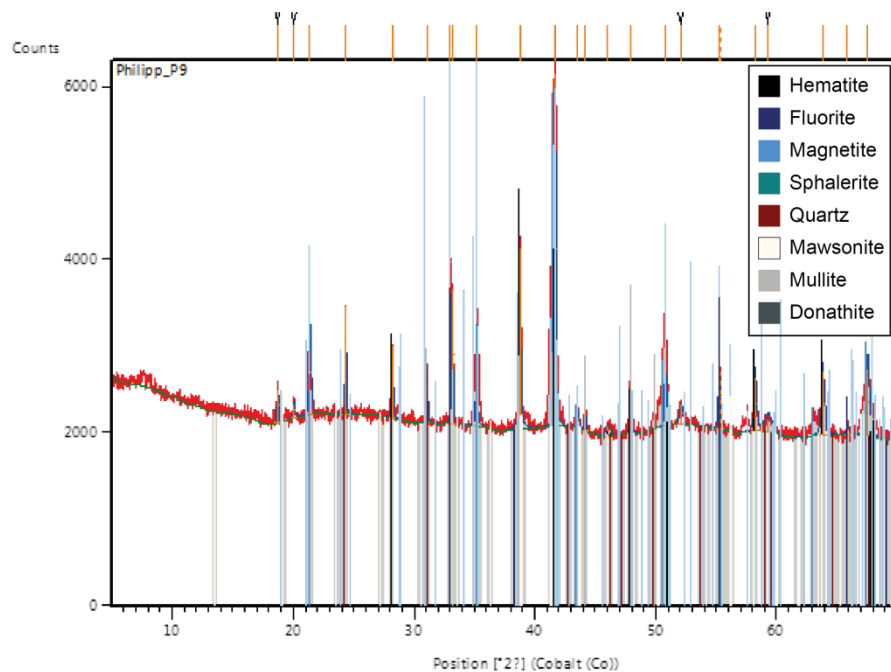


Figure 14: XRD pattern of sample 322.