Geological and mineralogical aspects on mineral carbonation

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Faculty of Science and Engineering
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Abstract

The mineralogical features that characterise each individual mineral and rock also influence every process they are part of. This is also the case with "the ÅA route" mineral carbonation method that has been under development at Åbo Akademi University for the past decade. The studies forming this thesis have been concentrating on specifying the geological and mineralogical raw material characteristics that need to be taken into consideration while this particular carbonation method is utilised.

The studies this thesis is based on include altogether 24 different samples of rocks and minerals. The first rock samples were collected at mines in Finland and also included mine tailings. Mine waste material was introduced to the study in order to state whether the produced rock material would make a suitable raw material and in order to map the economic benefit from using a readily quarried and ground material. Based on the results from the mine waste rocks, the studies were continued with serpentinite rocks and serpentine mineral samples. Samples were collected from mines and natural areas. A closer look at serpentinites and serpentines were necessary in order to resolve why the results varied drastically and which mineralogical characteristics were affecting the varying results. Results gained from the first and second studies indicated that the mineral structure was an issue, therefore the third study included mineral samples covering each Mg-bearing mineral from each silicate group.

The main method used in all the studies was the "the ÅA route" developed for carbon capture and mineralisation (CCM). The method is based on extraction and precipitation of magnesium and its fusion with carbon dioxide (CO_2) through an exothermic reaction. The Mg is extracted as ions and precipitated as magnesium hydroxide ($Mg(OH)_2$). The fusion with CO_2 results in a carbonate rock, magnesium carbonate ($MgCO_3$), also forming naturally all over the Earth as a result of natural carbonation processes. Before the experiments with "the ÅA route", the mineralogical features in each sample were studied with an optical microscope, Scanning Electron Microscope with Energy Dispersive X-Ray Spectrometer (SEM -EDX), X-ray fluorescence (XRF) and X-ray Diffraction (XRD).

All the results gained from the three separate studies support each other and give grounds to define the features essential for the successful utilization of "the ÅA route" method. Therefore this thesis supports these defining claims: a rock material suitable for mineral carbonation with "the ÅA route" should be an ultramafic phyllosilicate rock, descending from another phyllosilicate. The material should have at least 17 % Mg and it should contain over 10 % of

crystalline H_2O. If one feature does not meet the requirements but is close to the defined optimal value, it can be compensated by other positive features. Even though the experiments are focused on one particular carbonation method, there is no reason to state that the results could not be applied to other similar methods, as well.

By utilising carbonation methods such as “the ÅA route”, a safe and long-term storage option for the anthropogenic CO_2-emissions is created. Exploitation of waste materials as raw materials also solves other problems, as there is less need for waste storage and management. The produced end product also replaces the synthetically produced similar goods. In order to benefit from the excess waste minerals, rocks and gases, their characteristics need to be known. Therefore, it was essential to introduce a geological point of view to the “the ÅA route” in the form of this thesis.

Sammanfattning

De mineralogiska egenskaperna som är karakteristiska för enskilda mineral också påverkar de processer som mineralen används i. Detta gäller även mineralkarboneringsmetoden “the ÅA route” som har utvecklats vid Åbo Akademi under det senaste årtiondet. De studier som utgör denna avhandling koncentrerar sig till de geologiska och mineralogiska egenskaperna i råmaterialet, som skall iakttas vid kommissioneringen av “the ÅA route” –karboneringsmetoden.

Forskningarna som denna avhandling baserar sig på byggs på 24 stycken prov på bergarter samt mineral. Proven för den första studien samlades vid finländska gruvor och de omfattade både stenmaterial och anrikningssand. Orsaken till fokusering på gruvavfall var att ta reda på ifall gruvavfallet skulle kunna användas som råmaterial samt att studera hur stor ekonomisk nytta skulle kunna nås om man använder färdigt bruten och malt stenmaterial. På grund av resultaten som uppnåddes i den första studien, den följande studien fokuserade sig på serpentinitstenar samt serpentinmineral. Proven samlades från gruvor och vid naturliga områden. Den närmare studien på serpentiniter och serpentin gjordes för att utreda varför resultaten på dem hade så pass stor variation samt vilka mineralogiska egenskaper påverkade varieringen. Resultaten från den första och den andra studien indikerade att mineralstrukturen skulle spela en roll, varpå den tredje studien byggdes på prov som omfattade alla Mg-rika mineral från varje silikatgrupp.

Huvudmetoden som användes i varje studie var “the ÅA route”-metod, som utvecklades för att mineralisera koldioxidutsläpp (carbon capture and mineralisation, CCM). Metoden baserar sig på extrahering och utfällning av magnesium, vilken sedan förenas med koldioxid (CO_2) genom en exotermisk reaktion. Mg extraheras som joner och fälls ut som magnesiumhydroxid ($Mg(OH)_2$). När den förenas med koldioxid, produceras det en karbonatsten, magnesiumkarbonat ($MgCO_3$), som även uppkommer runtom världen genom naturliga karboneringsprocesser. Innan experiment med “the ÅA route”-metoden utfördes, de mineralogiska egenskaperna i varje prov studerades med ett optiskt mikroskop, svepelektronmikroskop (SEM -EDX), X-ray fluorescence (XRF) och X-ray Diffraction (XRD).

Resultaten från varje studie stöder varandra och således är det möjligt att definiera de egenskaper som är relevanta för att lyckas med tillämpning av “the ÅA route” –metoden. På grund av resultaten kan följande påstås: ett stenmaterial lämpligt för mineralkarbonering med “the ÅA route” skall vara en ultramafisk fyllosilikat som härstammar från en fyllosilikat. Materialet skall innehålla minst 17 % magnesium och minst 10 % kristallvatten. Ifall

en egenskap inte möter krav men har värdet nära det optimala gränsvärdet, kan det kompenseras med andra positiva egenskaper. Fast studierna i denna avhandling fokuserar sig på “the ÅA route” – metoden, kan resultaten anpassas till även andra liknande metoder.

Karboneringsmetoder, såsom “the ÅA route”, skapar trygga och hållbara förvaringsmöjligheter för de mänskliga CO_2-utsläpp. Utnyttjande av avfallsmaterial som råvaror även löser andra problem som uppkommer med avfallshantering samt -avlagring. Från avfallsmaterial producerade varor kan utnyttjas istället för liknande varor som nu produceras syntetiskt. Utnyttjande av övrigt avfallsmineral, -stenar samt -gaser kräver tillkännande av deras egenskaper. Således var det relevant att införa den geologiska synpunkten till utveckling av “the ÅA route” i form av denna avhandling.

List of publications

This thesis is composed of three studies, two of which have been published in scientific journals (II and III), and one in a conference proceeding (I). The scientific papers, listed below, are referred to in the text by their corresponding Roman numerals I-III. Papers I-III are reproduced by permission of the journals concerned.

I. **Suitability of Finnish mine waste (rocks and tailings) for Mineral Carbonation**
S. Sjöblom, O. Eklund
PROCEEDINGS OF ECOS 2014 - 27th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems. June 15th-19th, 2014, Turku, Finland, paper 244.

II. **The Significance of the Serpentinite Characteristics in Mineral Carbonation by "The ÅA Route"**
S. Lavikko, O. Eklund
International Journal of Mineral Processing, Vol. 152, pp. 7-15.

III. **The role of the Silicate Groups in the Extraction of Mg with the ÅA route method**
S. Lavikko, O. Eklund
Journal of CO_2 Utilization, Vol. 16, December 2016, pp. 466–473.

Contribution of the author

The author of this thesis was chiefly responsible for all the experimental work presented in these publications. The co-author participated in writing the papers. "The ÅA route" carbonation method discussed in each paper is developed at the Thermal and Flow Engineering Laboratory at Åbo Akademi University.

In addition to the publications listed, a number of non-refereed publications has been produced by or in collaboration with the author of this thesis, including conference proceedings and presentations.

List of abbreviations and symbols

AS	Ammonium sulphate
CCM	Carbon dioxide capture and mineralisation
CCS	Carbon dioxide capture and storage
CCSM	Carbon capture and storage by mineralisation
CO_2	Carbon dioxide
ESCA	Electron spectroscopy for chemical analysis
FeOOH	Iron oxyhydroxide (goethite)
GHG	Greenhouse gas
ICP-OES	Inductively coupled plasma optical emission spectrometry
IPCC	Intergovernmental panel on climate change
Kt	Metric kilotonne
LOI	Loss on ignition
$MgCO_3$	Magnesium carbonate (magnesite)
MgO	Magnesium oxide (periclase)
$Mg(OH)_2$	Magnesium hydroxide (brucite)
NH_4OH	Ammonium hydroxide
$(NH_4)_2SO_4$	Ammonium sulphate
pH	Potential of hydrogen
SEM	Scanning electron microscope
SEM-EDX	Scanning electron microscope energy dispersive x-ray spectrometer
T (°C)	Temperature (Celsius)
XRD	X-ray diffraction
XRF	X-ray fluorescence
ÅA/ÅAU	Åbo Akademi University
µm	Micrometer
ρ	Density

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Errata

Original publications

1 Introduction

1.1 Carbon Capture and Mineralisation

The main research question addressed in this thesis is related to anthropogenic CO_2-emissions that have been stated as one of the reasons for global warming (IPCC 2005). Carbon Capture and Mineralisation (CCM) has been developed to fix the CO_2 emissions into rock material (Seifritz 1990). This thesis focuses on the mineralogical characteristics considering the mineralisation of CO_2 with a CCM method "the ÅA route" (Fagerlund et al. 2010, Nduagu et al 2012b). The method is developed at the Thermal and Flow Engineering Laboratory at Åbo Akademi University. "The ÅA route" method is based on carbonation of Mg, which is extracted from silicate rocks and precipitated as magnesium hydroxide ($Mg(OH)_2$) (Figure 1) (Nduagu et al 2012b). Fusing the precipitated $Mg(OH)_2$ with CO_2 results in a carbonate mineral, magnesium carbonate ($MgCO_3$) (Fagerlund et al 2010). $MgCO_3$ is a natural mineral that can be used e.g. as building material (Gunning et al 2009).

Operating requirements for "the ÅA route" extend from technical operating to feedstock characteristics (Table 1) (Fagerlund et al 2010, Nduagu et al 2012b, I, II, III). In order to work optimally, the feedstock needs to be of certain fraction size (75 – 249 µm) (Fagerlund et al 2010, Nduagu et al 2012b). It needs to contain sufficient amounts of Mg (I) and it is beneficial to the extraction process if the rock/mineral has a high crystalline H_2O content (Nduagu et al 2012b), preferably > 12.5 % (I). Proportions of bulk rock material and ammonium sulphate (AS) ($[NH_4]_2SO_4$) are important (40g bulk rock material/60g AS) (Nduagu et al 2012b) in order to maximise extraction. Reaction needs to take place for 30 minutes (Nduagu et al 2012b). During the 30 minutes temperature needs to remain stable (Nduagu et al 2012b),

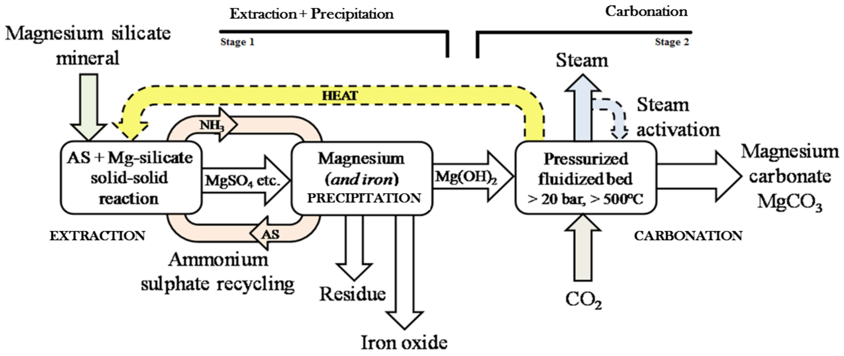


Figure 1. Process scheme for $MgCO_3$ production; extraction, precipitation and carbonation. (Modified after Nduagu et al 2012c).

Table 1. Key parameters and operating methods for “the ÅA route”.

Optimal fraction size (μm)	75 – 249
Optimal Mg content of bulk material (%)	> 17
Optimal H_2O content of bulk material (%)	> 12.5
Bulk rock/extraction agent ($[NH_4]_2SO_4$)	2/3
Operating time (min)	• 30 (extraction) • 10 (gas-solid carbonation) • 30 (aqueous carbonation)
Operating temperatures (°C)	• 480 (extraction) • 500 (gas-solid carbonation) • 30 (aqueous carbonation)
Carbonation method	Indirect
Pre-treatment of raw material	Mechanical

preferably at 480 °C (I). It is necessary to monitor the amount of ammonium hydroxide (NH_4OH) that is used for precipitation, as adding too much will precipitate Mg too early, together with Fe (Nduagu et al 2012b). Mg that is precipitated too early will be filtered out with Fe and less Mg is therefore left to be carbonated (Nduagu et al 2012b, I). Carbonation in the original “the ÅA route” manner requires a high temperature (500 °C) (Fagerlund 2012). Alternatively the carbonation can be executed as aqueous carbonation that requires a temperature of 30 °C (Björklöf 2010) and is therefore easier to use (Zevenhoven et al 2016).

As the requirements for the raw material are so specific, the choice of feedstock requires mineralogical identification (Nduagu et al 2012b). One good characteristic (such as high Mg %) does not guarantee a good feedstock if the raw material possesses characteristics otherwise unsuitable for “the ÅA route” (such as low crystalline H_2O %) (I, II, III). Processing non-optimal material increases production costs and results in excess energy consumption (Nduagu et al 2012a, 2012b, Fagerlund et al 2010). It is also essential to know how long the material maintains its suitability and what decreases the suitable characteristics (I). Unless the essential mineralogical characteristics are known and acknowledged, the method will not function optimally.

So far binding CO_2 with “the ÅA route” has produced promising results (Nduagu et al 2012a, Fagerlund et al 2010). Using ammonium salt ($[NH_4]_2SO_4$) and ammonium hydroxide (NH_4OH) for extraction of Mg is cost-effective, since NH_3 as well as SO_3 can be captured from the process and reused as ammonium salt (Figure 1) (Zevenhoven et al 2012). Energy for production of reactive magnesium can be obtained from the heat energy that the process generates (Figure 1) or from other industrial waste heat sources located near the suitable rocks/CO_2 source (Zevenhoven et al 2012, Romão 2015).

Managing the CO_2 emissions has resulted in studies and development of varying methods around the world (IPCC 2014). Some of the studies are of large scale while others are under development in a laboratory scale (Styles et al 2014, Gunning et al 2009). The methods can be indirect or direct, and some are aqueous while others are based on gas-solid reactions (Yan 2015). Methods may have one, two or multiple steps (Yan 2015).

There are methods similar to "the ÅA route", which is an indirect carbonation method (Fagerlund et al 2010). Another indirect multistep carbonation method studied by Wang & Maroto-Valer (2011) also uses ammonium salts, as does "the ÅA route". Their main material is serpentine, which has also been the main raw material for "the ÅA route" (Nduagu et al 2012b, I, II). Fraction size and use of NH_4OH for precipitation remind of "the ÅA route" (Fagerlund et al 2010, Nduagu 2012b). The main differences are capture of CO_2 from flue gas as the first step and differing operating temperatures (Wang & Marolo-Valer 2011). Another difference is that the original carbonation step of "the ÅA route" does not introduce additional H_2O (Fagerlund et al 2010). For Wang & Maroto-Valer (2011), a problem was acid recovery, which consumed much energy.

Lin et al (2008) had similar problems with chemical recovery. Their method also suffered from long processing times. Their processing time, temperatures and HCl as extraction agent differed from "the ÅA route". Otherwise their method resembled "the ÅA route" with serpentinite as raw material, indirect carbonation and two main stages (Fagerlund et al 2010, Nduagu 2012b).

Direct carbonation methods are an alternative to the indirect methods (Yan 2015) described above. They can use mechanical pre-treatment (e.g. Gerdemann et al 2007) as does "the ÅA route", but they can also use thermal pre-treatment (Chizmeshya et al 2002). The method of Chizmeshya et al. significantly differs from "the ÅA route", as their method requires removal of hydroxyl groups in serpentinites, while the presence of crystalline H_2O is essential for "the ÅA route" (Nduagu et al 2012b, I). This type of thermal treatment has been studied e.g. by Sanna et al. (2013), as thermal treatment is directly related to energy consumption. A problem with both Gerdemann et al. (2007) and Chizmeshya et al. (2002) was mainly the energy consumption.

Additional information on mineral carbonation studies can be found, for example, from the following references: Allen & Brent 2010, sequestering CO_2 by mineral carbonation; Aranda & Mastin 2016, carbonate production method utilising Al-rich materials with integrated CO_2 utilisation; Armstrong & Styring 2015, utilization and storage strategies for post-combustion CO_2 emissions; Bobicki et al. 2012, CCS with alkaline industrial waste;

Calera 2016, beneficial reuse of CO_2; Fabian et al. 2010, attrition milling on CO_2 sequestration on Mg-Fe silicate; Gunning et al. 2009, 2010, 2011, industrial waste and CO_2; Haug et al. 2010, leaching properties of olivine for carbonation purposes; Lacinska et al. 2013, serpentine minerals in CCSM; Munz et al. 2009, manufacture of magnesite and silica from olivine, CO_2 and H_2O; Pasquier et al. 2016, technical and economic evaluation of mineral carbonation process; Styles et al. 2014, variation in composition of ultramafic rocks and the effect for CO_2 sequestration following acid leaching; Teir et al. 2016, production of $CaCO_3$ from CO_2. Due to the different feedstock and operating requirements the studies above cover a wide range of rocks and minerals as well as varying methods. Therefore utilising CCM could be widely applicable around the world if the methods were commercialised.

Silicate rocks are potential CCM raw materials, as they form approximately 90 % of the Earth's crust (Deer et al 1992) and are therefore accessible around the world. There are several different types of silicate rocks (Deer et al 1992). They are divided into silicate groups, each group having its individual characteristics (Deer et al 1992). Most of the groups include Mg-rich silicate rocks (Deer et al 1992). Due to their different structures, molecular bonds and complexity, the different silicate rocks react differently when they are processed (Deer et al 1992, I, II, III). This complexity makes them a potential raw material for different methods, as a silicate rock with the most suitable characteristics may be chosen for each method (III). Choosing the most optimal raw material requires knowledge on both the method and the optimal feedstock (Nduagu et al 2012b, I, II, III). Silicate rock carbonation occurs as a natural process when silicate rocks weather and bind CO_2 in their lattice (Seifritz 1990, Deer et al. 1992), but it is possible to accelerate this process at processing plants (Gunning et al. 2009, Styles et al. 2014). Mining industry continuously quarries silicate rocks that do not have value as a metal ore but may be of value as potential raw material for mineral carbonation (I).

Papers I, II and III contribute to the development of "the ÅA route" method in a geological and mineralogical sense. However, the results are applicable to other purposes as well (II). Paper I discusses the possibilities for Finnish mine waste, rocks and tailings as raw material for CO_2 capturing. Paper II focuses on serpentinite rocks and serpentine minerals in order to unravel how their differences affect the process. Paper III concentrates on silicate structures and to what degree the location of Mg in the mineral lattice influences the extraction stage of "the ÅA route" method. Altogether, papers I – III produce a mineralogical database specifying the mineralogical characteristics that are essential and have to be taken into consideration when choosing raw material for mineral carbonation. The papers also discuss the problematics encountered during the mineralogical part of the experiments with "the ÅA route". In all the papers, the profitability and the economic point of view is kept in mind and discussed accordingly.

1.2 Why this study?

The background description is mainly based on Energy Visions 2050 (2009). The book describes the original problem with CO_2, alternative solutions and scenarios for the future.

Global warming is not a new phenomenon. The Earth has experienced fluctuation of its average temperature and, over time, nature has evolved to survive the alternating cold and warm climates. However, the industrial revolution resulted in conditions that both nature and people struggle with. Since the industrial revolution, the population of the Earth has expanded to over seven billion people (Worldometers 2015). Because of this, the demand for energy has grown. Up to 80 % of the world's energy production is based on the fossil fuels oil, coal and gas, which results in large CO_2-emissions spreading all over the globe. The pollution is concentrated around the polluting spots, but as the amounts are massive, the effects are detected worldwide. The secondary effects can be seen today as progressively occurring natural catastrophes such as hurricanes, floods and widening of the areas affected by draughts.

It is not only the warming environment but also the speed of the warming taking place that is problematic, as it leaves relatively little time for the environment to adapt. As the energy demand has multiplied over a relatively short period of time, the need to find new energy sources has accelerated. When the demand increased, the energy sources easiest to access were fossil fuels and they were harnessed in all the possible ways. As a result of the industrial revolution, the population expanded, which meant further energy demands. As the fossil fuels are mostly turned into energy by burning, it means that their components are chemically separated and form gases as well as polluting particles.

For decades, these gases and particles were treated as waste and dumped into nature and the atmosphere. As the amounts of these waste products were large, it did not take long before they started to alter the nature around them. What the users did not realise was the harm that was done to the atmosphere. The gases released by fuel burning displaced the natural gases in the atmosphere, resulting in pivotal changes on the Earth's surface. Solar energy that was previously largely reflected back to space by the natural atmospheric gases and the Earth´s surface is now further reflected by the industrial gases and particles in the atmosphere, preventing the additional energy from escaping. As the amount of solar radiation staying in the atmosphere rises, the environment absorbs more heat, raising the average temperature on Earth. Rising temperatures modify winds, currents and climate zones. As a result of climate change, the food crops are compromised as the rains are heavier or the rain season may not arrive in years, tides change causing floods and crop destruction, and the plants adapted to dominating weather conditions become extinct as the climate changes over a short period of time.

Pollution continues while the development of clean energy sources proceeds. The effects of climate change are discussed around the world. Regulations and goals of political bodies now force individual states to develop their energy production methods. Countries have their own regulations and, for example within the European Union, the goals are regulated and commonly shared. As the climate change issue becomes a shared concern, countries unite in order to reduce further damage. This cooperation has resulted in climate control agreements (IEA 2015, UNFCCC 2016) and their extensions, such as the Kyoto Protocol (IPCC 2007). Resources have been used to repair the damages and to invent new ways to produce energy. There are several resources for energy that are non-polluting and renewable, but harnessing them requires new methods. Unfortunately, a method development takes years, even decades, before it can be taken into use in a wide scale. Another problem for the development of the renewable energy sources is purely economic.

It is estimated that the fossil fuel resources will last from a few decades (oil and gas) to a century (coal), but only if the consumption remains on today's level. As the energy demand has been rising every year, it is difficult to estimate how long the easily accessible resources will last. As new methods to solve the climate change problem are developed around the world (Cuellar-Franca & Azapagic 2015), future technologies may develop enough for the fossil fuel usage to be fully converted into renewable energy source usage. As long as alternative energy sources are not covering the consumption, the most important action is to manage the produced waste and keep it from spreading into the environment. The most acute matter today is to restrain global warming and concentrate on managing the waste human activities produce. Implementing waste management is the most important measure to take as long as there are polluting energy sources in use. The safe and clean energy production will expand and be taken into use instead of the fossil fuels, and therefore, with time the need for waste management diminishes.

Minerals are valuable natural resources, and although they form the Earth, they are not renewable on a short time scale. Therefore, quarrying and consumption of rocks and minerals should be motivated. Minerals are a base for most of our everyday items, especially in industrial applications. Minerals carry the main components for our cell phones, computers, and even fertilisers that are essential for food production. Thus, excavation of this resource is also large. Minerals can be used in several different ways, also in reparation of the damage caused by humans. Because of the restricted reservoirs, utilising the leftover minerals is highly motivated. This is also the case in mineralisation of CO_2.

One option to utilise excavated areas is Carbon Capture and Storage (CCS). It is implemented in several countries as a solution but as it requires certain types of geological environments, it cannot be utilised everywhere (Figure 2) (IPCC 2005). It has also met opposition because of the risks of CO_2-leakage (Haug & Stigson 2016, Zevenhoven and Fagerlund 2010). Therefore, there has been a need for alternative methods such as CCM. In comparison to CCS, mineralisation has the benefit of stability and features as a risk-free option (Zevenhoven and Fagerlund 2010).

The more centralised the capture and the mineralisation of CO_2 is, the more cost-effective the whole process becomes. Therefore, it is beneficial to find CO_2 emitters and raw material providers that are located as close to each other as possible. In Finland, there are a number of mines located at or near the suitable raw materials for mineralisation of CO_2 (Figure 3) (Teir et al 2010, I).

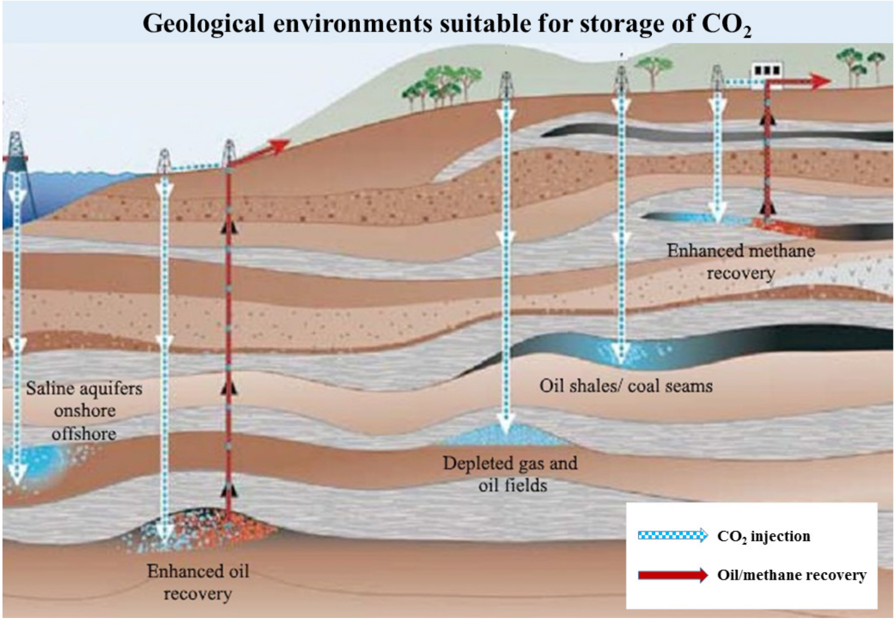


Figure 2. Suitable geological formations and enhanced industrial options for storage of CO_2. Modified after BCOG 2016.

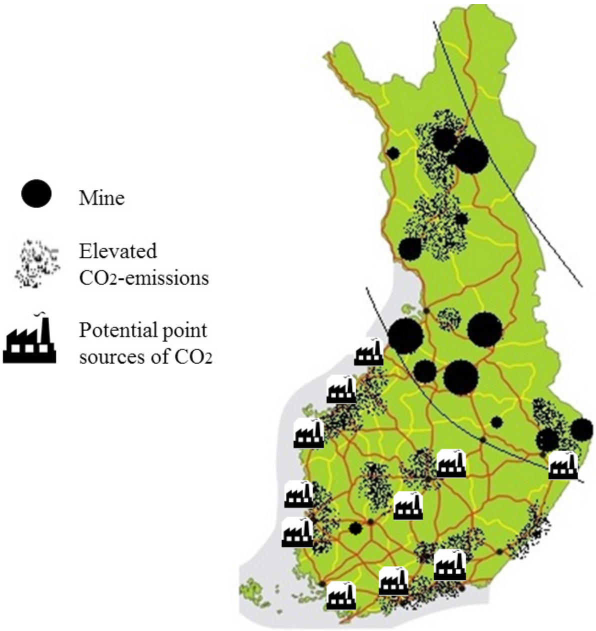


Figure 3. Map of Finland presenting the main road network, areas producing the highest CO_2-emissions, largest potential point sources of CO_2 and marking the mines located on or close to ultramafic areas. Ultramafic rocks are mainly located between the intersecting lines.

The largest CO_2 emissions are produced at fossil fuel power plants (each emitting on average 3001-4000 kt CO_2 per year) (Teir et al 2010, 2013). Another main producer is steel and iron industry (each emitting on average 1001-2000 kt CO_2 per year) (Teir et al 2013). Construction material production and pulp and paper industry are also significant emitters (each emitting on average 100-500 kt CO_2 per year) (Teir et al 2013). Most of the mines producing suitable raw material for mineral carbonation are located in the central and northern parts of Finland, while the largest of the emitters are located in the southern part of the country (Figure 3) (SVT 2010). Elevated CO_2-emissions in certain areas in Finland are partly a result of traffic (emitting ~20 % of Finland's CO_2-emissions), but in these areas there are also industrial CO_2 point sources available for carbon capture (Figure 3) (Teir et al 2013). The road network for transportation is comprehensive and, therefore, there is no need for additional road building for transporting raw materials to the polluters (Figure 3) (Teir et al 2010).

The most suitable location for a carbonation station would be close to the beneficiation plant. That would minimize the need for transportation after tailings are produced. Building a carbonation plant is a pricey investment, but if built properly, it only requires maintaining. Maintenance is cost-effective in the long run. Neglecting needed reparations would eventually lead to replacement of the whole system (Gunning et al 2010). When the mine is closed, a well-kept carbonation plant can be dismantled and further relocated (Kumar et al 2010, Heikkinen et al 2005). Capturing CO_2 is the most expensive part of CCM (Teir et al 2010). Therefore, cost-effective capture of CO_2 requires a source that has high concentration of CO_2 in the produced gas stream. Low CO_2 concentration results in higher energy consumption, as it is more labour-intensive to capture the wanted percentage of produced emissions.

With the latest capture methods it is possible to capture up to 90 % of the CO_2-emissions that fossil fuel power plants produce, but the capturing process doubles the energy costs (Teir et al 2010). Alternative energy sources with lower cost or a more economical capturing method is required before capture of CO_2 can be applied to air polluting power plants (Teir et al 2010, Zevenhoven et al 2008). The most economical solution would be to avoid the capturing step as a separate process altogether, and instead, execute the carbonation with flue gases containing CO_2 (Romão 2015).

If a CO_2-producer is located near a mine with a carbonation plant, the transportation costs are minimal. Otherwise, transporting CO_2 is most practicably done by pipeline or ship (Teir et al 2010). Within Finland, ship transportation is not an alternative unless the capture and mineralisation are both done at locations along the coast (Teir et al 2010). Pipeline construction between raw material providers and CO_2 emitters is a possibility only if both producers are large enough and planned to be in business for a long period of time.

CO_2 is typically transported compressed, if transported by pipelines, and in liquid form, if shipped or transported on land by road. The amount of CO_2 that needs to be transported is significant. Transporting large amounts of compressed or liquefied gas is a potential risk that may not be acceptable. The capacity for transportation is low, at least since environmental issues have to be taken into consideration. Neither does transportation by railway provide the needed capacity in large scale and can only be considered locally, as some mines already use railways to transport their products (Teir et al 2010).

The carbonated end product can be piled up by the mine the same way barren ore would be piled and later landscaped as the mine is to be closed. As the transportation distance is short the costs can be minimised. These reservoirs can later be used, as weathering of carbonate rocks is slow (Gunning et al 2010). However, before rocks are covered up and landscaped the further usage should be determined in order to avoid unnecessary energy consumption of covering and then excavating the material again (Heikkinen et al 2005). The transportation of the end product is safe as carbonate rocks are stable and non-toxic. Further use of the produced carbonate rocks within suitable industries is preferable as it is a profitable option (Gunning et al 2010).

2 Aim of the research

The aim of Papers I, II and III is to define which Mg-bearing minerals and rocks can be used to bind carbon dioxide with "the ÅA route". Another aim is to determine why it is possible to extract Mg for the carbonation reaction from some materials but impossible from others. It has, therefore, been essential to define how the origin of a rock influences the mineral carbonation process and what causes one rock type to react better than another type with equivalent amounts of Mg. An important outcome of the project is a comprehensive compilation of the mineralogical features that are critical for carbonation processes. This thesis contributes to minimising the economic and health concerning risks the carbonation application has when it is harnessed by operators, for instance mines.

The main focus in this thesis is to (1) evaluate whether rock materials from Finnish mines would be suitable as raw materials (Paper I), (2) explain why rocks with similar structural features and chemical formulae behave differently in "the ÅA route" process (Paper II) and (3) how the mineral structure influences extraction of Mg (Paper III).

Previous studies on the development of "the ÅA route" have focused on the technical side of the method (Fagerlund et al 2010, Nduagu et al 2012b, Romão 2015, Zevenhoven et al 2012). This thesis provides the development of the method with geological, mineralogical and petrological views. Even though this study has concentrated on mineralogical features, it has contributed to the technical development as well by reporting methodological remarks and concerns.

This thesis is also a contribution to the global research on developing methods to capture anthropogenic CO_2-emissions and, thus, control global warming. Even though this PhD-project has been conducted with "the ÅA route" in mind, the results could most likely be applied to other methods as well. All mineralogical knowledge is not only useful but could be crucial when raw material for carbonation is selected, regardless of the method.

3 Material

The study is built around ultramafic (< 45 wt% SiO_2) rocks and minerals that have high MgO content (Nduagu 2012b, I, II, III). Most of the rock samples are collected at mines, while the mineral samples are collected from appropriate field areas (I, II, III) (Appendix A). The geological and mineralogical features that are acknowledged and measured are the major elements, crystalline H_2O, crystallographic structure, metamorphic grade and the geological origin of the samples. Altogether 21 samples are included in the mineralogical studies and the processing studies (Appendix A, Appendix B). Some of the mineral samples display a chemical composition close to the ideal formula, while others display larger variation (Table 2). The number of collected samples was originally higher, but samples deemed unsuitable during the preliminary mineralogical survey were excluded from further studies.

Material gathering is focused around mine waste especially in Papers I and II. The usage of predominant mine waste material is based on the profitable advantage and easy access to the material. The mine waste used for the studies, and potentially useful in the full-scale mineral carbonation process, is already quarried and in some cases also ground, which might make exploitation cheaper (I). However, the ore enrichment process introduces salts and acids to the tailings, which are thus fused with unsuitable chemicals (I). In contrast, the waste rocks do make an exploitable raw material for carbonation, provided that their characteristics are found suitable for the process (I). Paper II also includes results on pure serpentine minerals defining the essential features found on serpentinites. Paper III is focused on the mineralogical features of pure silicate minerals free from contaminants or other impurities that otherwise have a distorting influence.

The thesis is largely built around serpentinites and serpentine minerals, as they have been found to be highly suitable for carbonation (Nduagu et al 2012b, Lacinska et al 2013). However, the features making them suitable were not known and, therefore, several varying samples from serpentinite rocks and serpentine minerals have been analysed (Papers I and II). The results show that it was absolutely necessary to define their characteristics further.

The samples are labelled in a way to make it easy to distinguish them from each other. In Paper I, the name represents the mine from which the sample is collected, and as there are several samples from the same mines, they are additionally marked with a running number. Tailing samples are indicated by an R at the end of the labelled name. In Paper II, the sample name indicates whether the dominating mineral in the sample is antigorite or lizardite and the end letter shows the country the sample originates from. In Paper III, the name consists of the mineral name and the number referring to Paper III in this thesis. The talc samples originating from the same area are distinguished from each other by lower case letters indicating the texture of the sample.

Paper I focuses on the usability of mine waste material for carbonation, Paper II on the essential features of serpentinites and serpentine minerals, and Paper III on how the CCM-process is influenced by the specific features of the silicate group minerals.

Table 2. Examples of chemical compositions of different Mg-bearing (wt%) silicates. (webmineral.com)

	Phyllosilicates				
	Serpentine group		Clay mineral group		Mica group
	Lizardite	Antigorite	Talc	Vermiculite	Phlogopite
	$Mg_3Si_2O_5(OH)_4$	$(Mg,Fe)_3Si_2O_5(OH)_4$	$Mg_3Si_4O_{10}(OH)_2$	$(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2\cdot 4H_2O$	$KMg_3(Si_3Al)O_{10}(F,OH)_2$
SiO_2	43.36	39.95	63.37	43.48	42.99
TiO_2					
Al_2O_3				11.92	12.16
FeO		17.92		12.82	
MgO	43.63	30.15	31.88	14.39	28.84
CaO					
K_2O					11.23
Na_2O					
F					4.53
H_2O	13.00	11.98	4.75	17.87	2.15

	Nesosilicates		**Inosilicate**	**Cyclosilicate**
	Olivine group	Garnet group	Pyroxene group	6-member ring
	Forsterite	Pyrope	Augite	Cordierite
	Mg_2SiO_4	$Mg_3Al_2(SiO_4)_3$	$(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$	$(Mg,Fe)_2Al_3(AlSi_5O_{18})$
SiO_2	42.71	44.71	48.3	51.36
TiO_2			3.38	
Al_2O_3		25.29	8.63	34.86
FeO			6.08	
MgO	57.29	29.99	15.35	13.78
CaO			21.35	
K_2O				
Na_2O			1.31	
F				
H_2O				

3.1 Paper I sample overview

The 14 samples presented in Paper I are all waste material from Finnish mines (Appendix A, Appendix C). The excluded samples (Talvi1, Talvi2, Talvi3, Pam2) did not contain any Mg, which is a prerequisite for CCM following "the ÅA route". The collected samples included both waste rocks and mine tailings.

The Hit-samples are collected from a nickel mine situated in a large serpentinite body (Hitura). The host rock to the mineralisation is dominated by massive serpentinites with thin veins of calcite and pure serpentine minerals. The Kev-samples are from a poly-metal mine situated in an olivine-pyroxenite (Kevitsa). The Pam-samples originate from a gold mine located in talc-chlorite schists (Pampalo). The Polvi-samples are from a talc mine with very pure talc (Polvijärvi) and the Talvi-samples are collected from a nickel mine that operates on mineralised black schist (Talvivaara).

3.2 Paper II sample overview

The samples for Paper II feature different types of serpentinites and serpentine minerals (Appendix A, Appendix C). They were collected from either mines or outcrops.

Samples AntN and LizN originate from the Modum area in Norway. These magnesite-serpentinite deposits are situated in amphibole-dominating rocks (Raade 1986). AntN is collected from a serpentinite deposit dominated by antigorite and LizN is from a deposit dominated by lizardite (Raade 1986). In AntN, bastite is the most dominating texture, whereas the most dominating textures in LizN are mesh and sheafiness. Based on their textures, both samples from the Modum area have been serpentinised from amphibole rich parental rocks (Deer et al 1992). The samples also display pyroxene relicts.

Sample AntF is collected from a serpentinite at the Hitura mine, Finland. The sample is from an antigorite seam displaying a columnar habit, and it is dominated by blurred olivine pseudomorphs and spherulites as well as mesh texture. Sample LizIT originates from Elba Island, Italy. The sample is highly dominated by pure, rounded lizardite grains. Sample SerpS is from Piteå mine, Sweden. It is dominated by mesh texture and has a high crystalline H_2O wt% of 15.15 wt%. Based on the textures, samples AntF, LizIT and SerpS are formed from olivine dominating parental rocks (Deer et al 1992).

3.3 Paper III sample overview

The samples for Paper III are selected on the basis of the presence of Mg-bearing minerals belonging to different silicate groups (Appendix A, Appendix C). The samples are collected from mine sites and outcrops.

Samples representing the phyllosilicate group are 3TAc, 3TAs, 3VE and 3BI. Samples 3TAc and 3TAs originate from Polvijärvi mine located within a large talc dominating body in Finland. The c-sample represents an unstrained crystalline talc and the s-sample a sheared talc. The sample areas are located close to each other, however, the unstrained crystalline sample is from a section that has not been affected by deformation and the sheared sample is from a shear zone. Sample 3VE originates from the regolith of the Sokli carbonatite intrusion, northern Finland. It consists to 95 wt% of pure vermiculite mineral (5 wt% consisting of carbonate build up between the sheets) and has a high H_2O wt% (15.34 wt%). Sample 3BI is from Skräbböle, Parainen, Finland. It is a phlogopite mica with 27.39 wt% MgO. Samples 2VE and 3BI have similar mineral structures but their crystalline H_2O content is significantly different from each other, 3BI containing only 1.1 wt% crystalline H_2O in its mineral lattice.

Samples representing the nesosilicate group are 3OL and 3PY. 3OL originates from Åheim, Norway and consists of forsteritic olivine. It only contains 0.58 wt% crystalline H_2O in its mineral lattice. Sample 3PY is collected at a pyrope mine located in Podsedice, Czech Republic. The garnet from this locality has high Mg content. The sample is composed of a very pure pyrope mineral and no inclusions were detected in the samples that were used for the experiments.

The 3KO sample represents the cyclosilicate group. It is from Kiuruvesi, Finland and represents a very pure cordierite mineral with only 1.63 wt% crystalline H_2O in its mineral lattice.

4 Methodology

Mineralogical characteristics of Mg-bearing phases and their application for CCM are the focus in this thesis, therefore characterisation of each sample has been executed with care. The same basic methodology was applied throughout Papers I-III. Thin sections were prepared for each sample and the mineralogy and texture were studied with optic transmitted light microscope. After the thin sections were mapped and documented, sample surfaces were analysed with a Scanning Electron Microscope Energy-dispersive X-ray spectroscopy (SEM-EDX). After these mineralogical analyses, it was determined whether the samples were non-hazardous and suitable for further studies. Preliminary characterisation was particularly necessary with the samples presented in papers I and II as they include serpentinite samples which may contain detrimental asbestos minerals. Papers I and II discuss rock material rather than pure minerals. Mineral phases present in rock materials were obtained with X-ray Diffraction (XRD). Chemical compositions for each individual sample (I–III) were determined with X-ray Fluorescence (XRF), except for one sample (AntF) in paper II, where the composition was determined with SEM-EDX due to a small sample size.

Crystalline H_2O content in the samples was obtained by measuring the loss on ignition (LOI) in each sample. The values were used for normalising the compositional measurements received from XRF-analysis. For the measurements, some sample material was ground to <10 µm and dried overnight (min. 8 hours) in order to vaporise surface moisture. Three grams of dry material was then heated at 1050 °C for 60 minutes, cooled for 10 minutes and weighed. Weight difference was subsequently used for calculating the percentage of crystalline water in each sample.

4.1 Sample preparation

Before Mg-extraction experiments, the rocks were first crushed, grinded and sieved to a sand material. Based on Fagerlund et al (2010) the fraction of 75 – 124 µm fraction was chosen to be used for all experiments. However, due to the limited amount of material, the experiments in paper III were conducted with the fraction size 75 – 249 µm (Fagerlund et al 2010, Nduagu et al 2012b). Based on previous results (Fagerlund et al 2010), the difference in the fraction sizes is not significant enough to compromise the results. That can, thus, reliably be compared to the experiment on the smaller grain-size.

4.2 Experimental work

All the experiments were executed by using the mineral carbonation method "the ÅA route", developed at Åbo Akademi University. With this method, the Mg content of the raw material is extracted and then precipitated as $Mg(OH)_2$. The produced magnesium hydroxide can subsequently be fused with CO_2 through an exothermic reaction. The final product is a carbonate rock, magnesite ($MgCO_3$). The whole "ÅA route" process was executed to the end only in paper I. Papers II and III focused on the extraction and precipitation as the mineralogical problematics were located in those two parts.

4.2.1 Extraction and precipitation

Mg was extracted by heating 40 g raw material together with 60 g ammonium sulphate ($[NH_4]_2SO_4$). This was done in a rotary oven for 30 minutes. The resulting mixture was then dissolved in distilled water and insoluble material was filtered out. The remaining liquid containing the extracted ions (mainly Mg and Fe) was subsequently carefully treated with ammonium hydroxide (NH_4OH). As pH was rising, it was possible to precipitate and collect the solid goethite ($FeO[OH]$) at pH ~8.5. After removal of Fe, by raising the pH brucite ($Mg[OH]_2$) was precipitated. Full precipitation of brucite required a pH above 11.

The first study (paper I) included temperatures of 440 °C and 480 °C, a recommendation by Nduagu (2012a), and each sample was experimented on with both temperatures. This was done in order to study the ideal temperature for the process. Based on the results from paper I, further experiments were only conducted in 480 °C (papers II and III).

4.2.2 Carbonation

The second stage of "the ÅA route" considers the carbonation of brucite that was precipitated during the first stage. Brucite was fused with CO_2 in a pressurised fluidised bed and the reaction produced a carbonate, magnesite ($Mg(CO_3)$ (Fagerlund 2012). As the carbonation through "the ÅA route" requires high temperature and pressure (Fagerlund 2012), another carbonation method was also used. This wet carbonation method was executed in 30 °C and atmospheric pressure (Björklöf 2010). The results were similar for both methods.

4.3 Mg-analysis

Following the magnesium throughout the process was the main concern. Mg was monitored both visually and instrumentally (Figure 4).

4.3.1 Before the processing

Measurements by XRF- and SEM-EDX-analyses defined the amount of Mg in each studied rock or mineral. Even for heterogeneous samples, the exact location of Mg in a sample was possible to detect. The measurements gave information on the Mg-percent in the raw sample, how Mg was distributed and, on heterogeneous samples, where it was mostly located.

4.3.2 Mg-analysis during the processing

10 ml liquid samples were collected throughout the precipitation process. The liquid samples were analysed with ICP-OES, in order to monitor how much Mg was present in the beginning, after precipitation of FeOOH, and in order to examine whether there was any Mg ions left in the liquid after the precipitation of $Mg(OH)_2$. Determining the ideal pH was essential as the aim was to precipitate pure $Mg(OH)_2$ without contaminants like Fe. As precipitation of FeOOH and $Mg(OH)_2$ tended to overlap, analyses of the liquid samples were essential. When pH was increased, the most indicative sign of reaction was the change in colour (change from clear to yellow/dark green/red nuances for Fe and clear to white for Mg) and the appearing cloudy precipitates. Therefore, continuous ocular monitoring was important.

4.3.3 After the processing

Most informative results were gained by analysing the processed insoluble material and comparing the results to the unprocessed material. The percentage of Mg was measured on both the start and the end product, and the difference shows how much Mg was extracted. For the samples that successfully donate their Mg, it was also possible to optically detect the depletion by analysing the sample with a stereomicroscope. The purity of the produced $Mg(OH)_2$ was confirmed with XRD, in order to ensure that there were no significant amounts of Mg precipitated in form of the less reactive MgO (Fagerlund et al 2010).

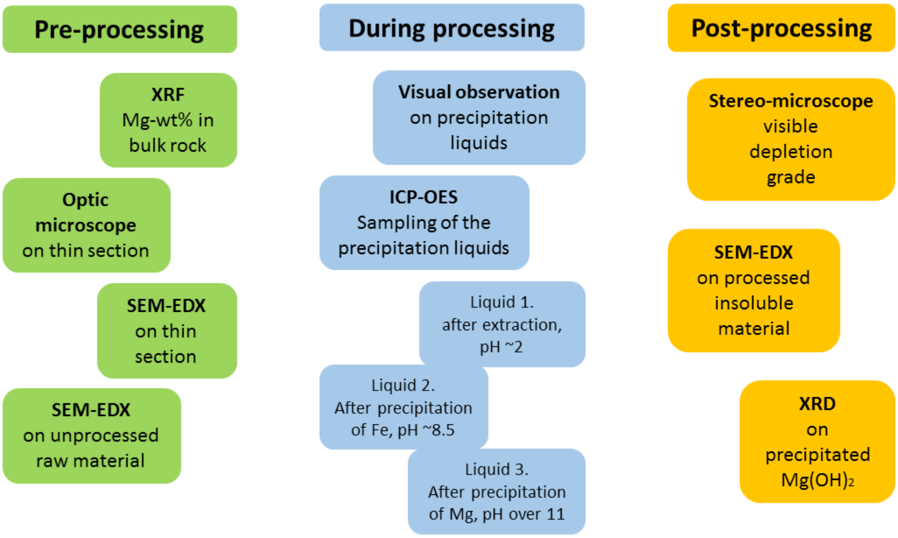


Figure 4. Mg-analysis methods before, during and after processing.

5 Results and discussion

Based on Papers I-III the key findings influencing “the ÅA route” are: (a) Minimum Mg content of a rock or a mineral, (b) influence of the amount of crystalline H_2O found in mineral lattice of the raw material, (c) origin of the parental rock, (d) metamorphic alteration of the rocks and (e) effects of individual structural characteristics in a rock or a mineral (Table 3). Key findings also include amounts of SiO_2 and Fe, adequate processing time and temperature as well as extraction success (Table 3). Based on the findings a flow chart was created to display the essential mineralogical characteristic that should be acknowledged during a carbonation process (Figure 5). Each of the papers I, II and III concentrates on specific findings but the observations do partly overlap and support each other.

Table 3. Key findings of Papers I-III.

KEY FINDINGS	
Mg content	Raw material should contain at least 17 wt% MgO
Crystalline H_2O content	Raw material should contain at least 12.5 wt% crystalline H_2O. Presence of crystalline H_2O supports the extraction process.
SiO_2 content	SiO_2 content of the raw material should not exceed 45 wt%.
Fe content	Fe should be carefully removed before precipitation of Mg. Fe may appear as contamination during carbonation if it has not been properly removed during earlier stages.
Structural complexity	Extracting Mg from sheet silicate structures is easier than extraction from chain silicate and ring silicate structures.
Protolith	Serpentinite rock descending from a dunitic parent rock makes a more successful raw material than a rock descending from other peridotite protoliths.
Metamorphic grade	Processing high grade rocks requires more energy in comparison to low grade rocks.
Time	Extraction time of 30 minutes is adequate. Extraction during 30 minutes is successful with suitable materials.
Temperature	Processing temperature of 480 °C produces significantly better results than processing temperature of 440 °C.
Extraction	Highest Mg-extraction % obtained is ~80 % (vermiculite mineral). Lowest extraction % obtained is 0 % (pyroxenite, andesite tuff, iron formation, cordierite).

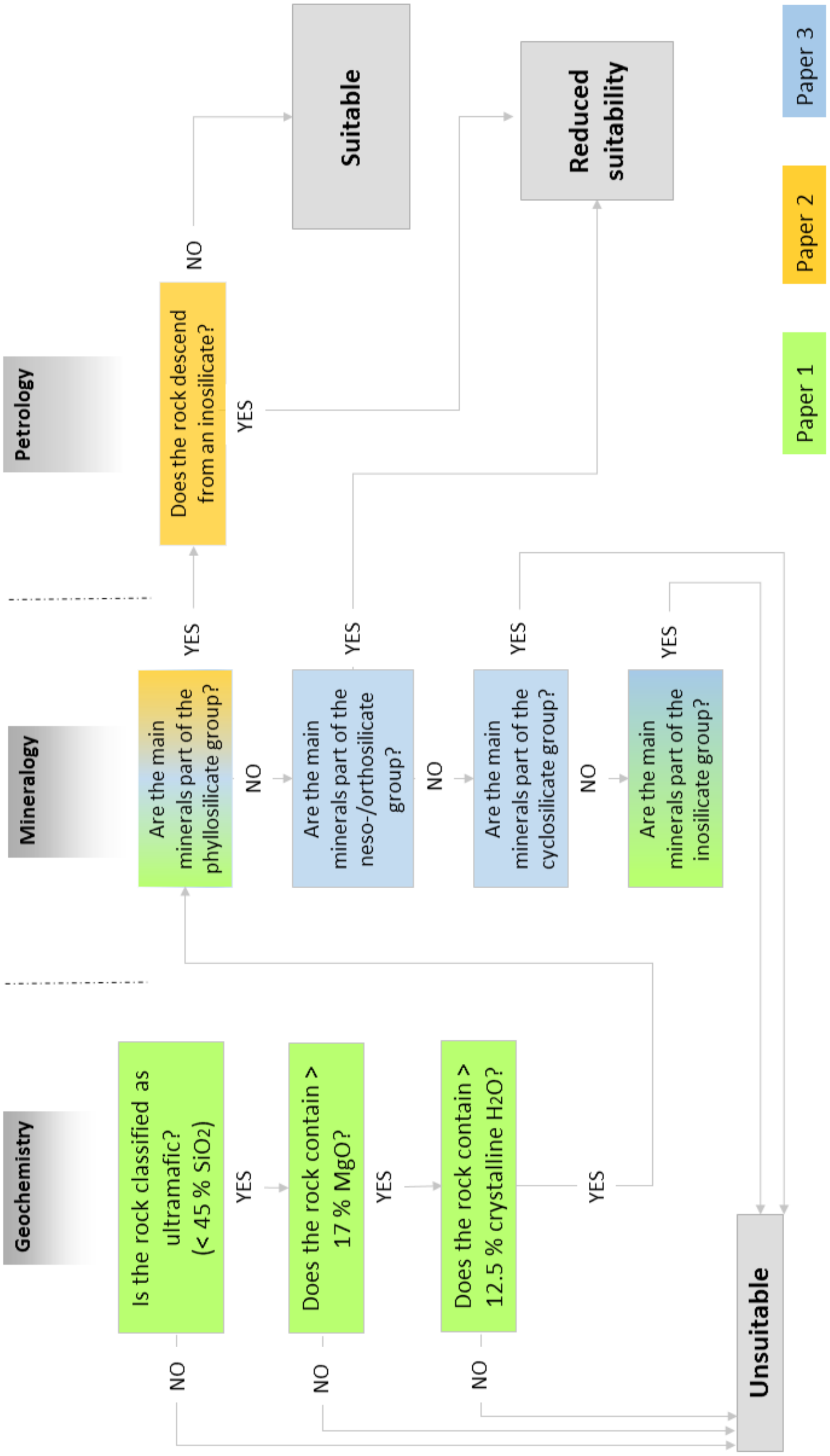


Figure 5. The essential mineralogical characteristics that should be taken into consideration in mineral carbonation.

Paper I focuses on the minimum amount of Mg wt% in rocks that is required in order to produce profitable amounts of $Mg(OH)_2$ to be carbonated, as well as the minimum necessary amount of H_2O bound in the mineral lattice of hydrous minerals. The studied rocks that contained a minimum of 17 wt% were all ultramafic. The rocks that produced sufficient amounts of $Mg(OH)_2$ all contained more than 12.5 wt% crystalline H_2O, which was therefore concluded to be the minimum required amount. The samples with the minimum required amount were serpentinites and a talc-chlorite schist. Other major findings considered the time serpentinite mine waste material is usable, unexpected problems caused by the ore processing chemicals found in the tailings, favourable extraction temperatures (~480 °C) and locating a fundamental problem in the process (low extraction). In general it can be stated that mine waste material is a suitable source of raw material for CCM. Results of rock and tailing materials are comparable but the tailing processing material may include hazardous substances.

The major finding in Paper II is the influence of the origin of a rock. The conclusion is that a serpentinite rock or a serpentine mineral that originates from a dunitic parent rock is more suitable than a serpentinite or serpentine mineral that has inosilicate bearing peridotite protoliths. The serpentinisation process does not alter the minerals throughout, relicts of an inosilicate are transferred into the serpentinite or serpentine mineral, which further controls the final mineralogical structure with preserved relicts of pyroxenes (inosilicates) in the serpentine (phyllosilicate). Another notable finding is the difference between serpentine minerals antigorite and lizardite; even though both can be used as raw material in CCM, lizardite contains more of the favourable features, such as simpler mineral structure and higher MgO wt%, in comparison to antigorite.

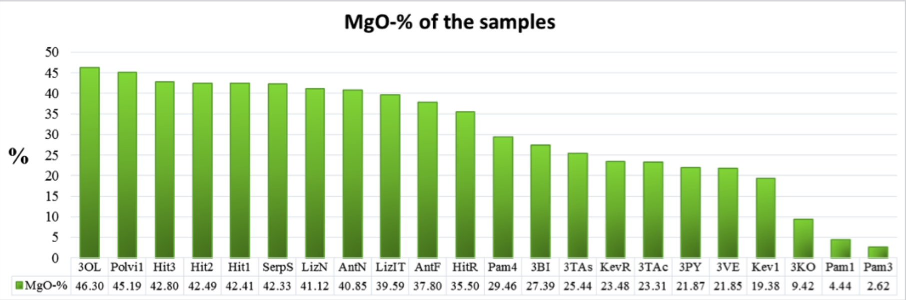
Paper III verifies and specifies the phyllosilicate group as the most suitable raw material. Other tested Mg-bearing silicate group minerals produce either low or poor results. Nesosilicates may be a potential raw material when the process is optimised, while the ino- and cyclosilicates are concluded to be unsuitable even for an optimised “ÅA route” process. The role of the crystalline H_2O is specified further, as the results indicate that a high percentage enhances the extraction process. However, a low H_2O content can be compensated, to a certain degree, with other features such as simple crystal structure, weak bonds and the accessible location of the Mg ions.

5.1 Mineralogical observations

Based on Paper I, the amount of Mg present in rocks and minerals has to be high enough in order to produce profitable results. Most of the samples in Papers I-III exceed the minimum required Mg content of 17 wt% (Figure 6). (Some samples have lower Mg content but were included based on other possibly favourable features, such as silicate group or high H_2O wt%.) Results from Papers II and III show that a high Mg content alone does not necessarily make a material suitable if the Mg cannot be efficiently extracted from the raw material. (Based on results from Papers I-III, a sample with lower Mg content can precipitate more $Mg(OH)_2$ than a sample with higher Mg content.) There are also other features related to the raw material that influence the final profitability (II, III). Thus, Mg content of the bulk rock/mineral alone cannot be used to determine whether a rock is profitable raw material.

Results in Paper III indicate that mineral structure and where in mineral lattice Mg is bound have an important role in efficient extraction. For most of the samples, ammonium salt reacts with the surface of the mineral grains (Romão 2015). An exception is the sheet silicate sample (III), where ammonium salt can reach and break the weak Wan der Waals bonds between hydrous T-O-T sheets and, thus, create more extensive reaction throughout the mineral. In other samples mineral-AS reaction seems to be restricted to the mineral surface only (Romão 2015, III).

In silicate minerals, Mg ions are usually found in the octahedral site of the lattice. However, the ability for Mg to be released from the lattice is dependent on the silicate group. In neso-, cyclo- and inosilicates, Mg is situated in the octahedral site sharing six oxygen anions through strong bonding that does not easily emit Mg from the lattice (Figure 7 a). In phyllosilicates, Mg is situated in the octahedral site, but with brucite coordination ($Mg[OH]_2$), meaning that Mg is connected to OH anions that are easier to break than O anions (Deer et al 1992, Nduagu et al 2012b, III). Thus, Mg is easier to extract.



	3OL	Polvi1	Hit3	Hit2	Hit1	SerpS	LizN	AntN	LizIT	AntF	HitR	Pam4	3BI	3TAs	KevR	3TAc	3PY	3VE	Kev1	3KO	Pam1	Pam3
🟩MgO-%	46.30	45.19	42.80	42.49	42.41	42.33	41.12	40.85	39.59	37.80	35.50	29.46	27.39	25.44	23.48	23.31	21.87	21.85	19.38	9.42	4.44	2.62

Figure 6. MgO content of the study samples.

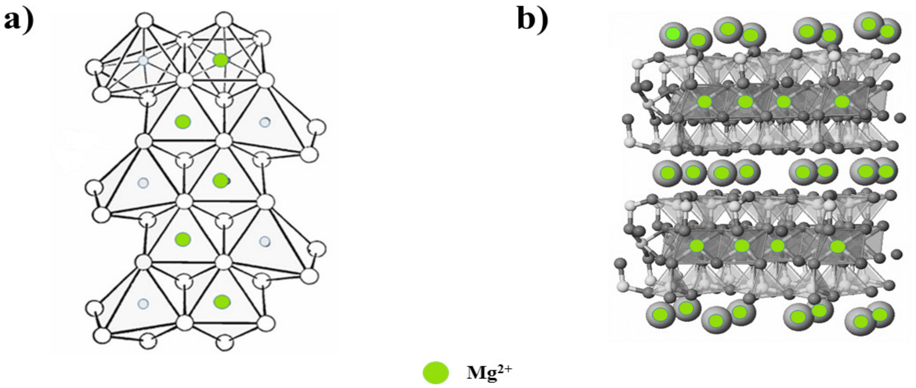


Figure 7. The location of Mg in a) chain silicate (octahedral site) (amphibolite) (modified after http://minerals.gps.caltech.edu) and b) sheet silicate (octahedral site/hydrous interlayer) (vermiculite) (modified after illinois.edu).

In vermiculite, Mg is additionally situated in the hydrous interlayer site as hydrated Mg (Figure 7 b) from where Mg is even more easily emitted (III). This hydrous sheet silicate structure yields the best results (I-III).

Results from Papers I-III support and develop further the previous conclusions considering the role of crystalline H_2O in the CCM-process (Nduagu et al 2012b, Fagerlund 2012). Rocks and minerals with high H_2O content tend to work better in the process, as their Mg content is more easily extracted (Nduagu et al 2012b, I, II, III). For most of the samples, the amount of crystalline H_2O is directly related to the successfulness in the process (I). The presence of OH^- molecules in the mineral lattice makes it easier for the ammonium salt to break the bonds of the Mg ions (I, III). If there are no OH^- molecules present, the structure may inhibit the extraction (III). This is evident when comparing the dry olivine to the wet serpentinites (I, II, III). Despite their mineralogical similarities, the dry olivine sample (Figure 8) performed relatively weakly (III) while the wet serpentinite samples performed well (I, II), even when other characteristics reduced the performance of the latter. Another exemplary result was also reached with vermiculite and biotite, which are both micas with sheet structures (III). Mg in both samples is connected to OH anions in the octahedral site of the T-O-T layer (in vermiculite also in the interlayer), but biotite has a lower crystalline H_2O content (max. 4 wt%, Deer et al 1992) (Figure 8). The results show that biotite produces significantly less $Mg(OH)_2$ than vermiculite (III). However, the biotite structure clearly compensates for the low content of crystalline H_2O, as the amount of Mg extracted is satisfactory (III). Observation of other negative features compensating for the positive effect of the crystalline H_2O is also discussed in Paper II. It is shown that the serpentinite samples with the

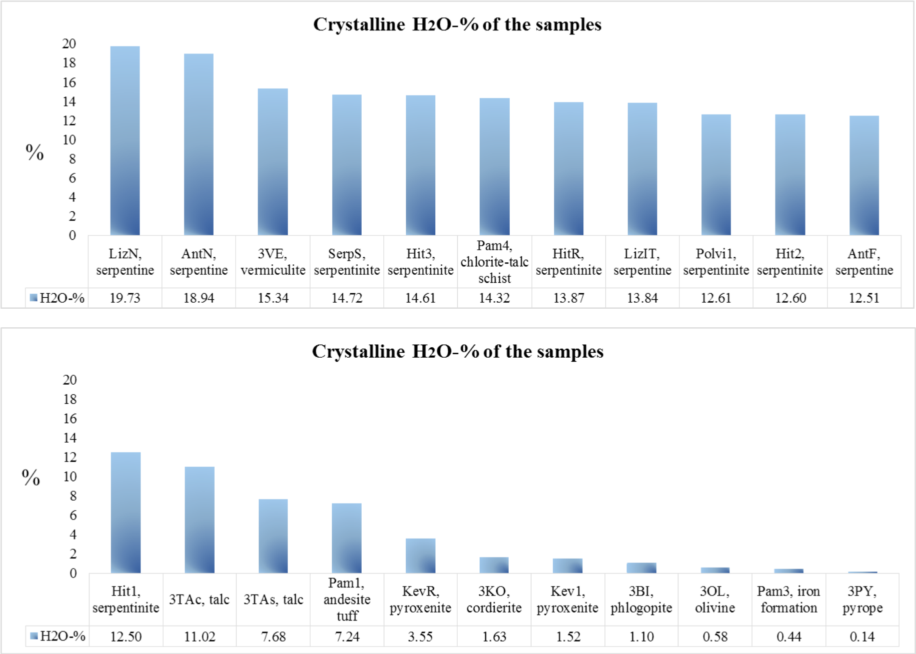


Figure 8. The amount of crystalline H_2O in the samples (measured as LOI).

highest amounts of crystalline H_2O performed the weakest, which is directly related to their mineralogical origin (II).

Both Papers I and II include several samples of variable serpentinites and serpentine minerals. An economically interesting result is that the grade of weathering or other alteration, related to for example mining, does not influence the performance of the samples (I). This is a valuable finding considering profitability. There are no differences in the results between the different Hitura serpentinite samples despite the severe variation in the degree of weathering. Based on the results, serpentinite gangue is usable for mineral carbonation even if it has been piled up for 15 years or more. The main result for serpentinites and serpentine minerals is that their origin is of utmost importance for their suitability in “the ÅA route” method. The large variability between the samples is directly comparable to the subsequently serpentinised parent rock. The samples originating from dunites donate their Mg significantly better than the samples originating from other types of peridotites (II). The parent rock can be determined from their texture and mineralogy (II). Previous studies (I, Byggmästar 2011) have shown that metamorphosed ultramafic rocks that, additionally to serpentine, also contain pyroxenes and amphiboles, give a low Mg yield. It was therefore expected that serpentinites from other peridotites than dunites have reduced suitability. On pure mineral level, serpentinite features that have a positive influence on the process are more common in lizardite-mineral than antigorite-mineral: theoretically, lizardite only contains Mg and Si in addition to H_2O, while antigorite also contains Fe (II). Due to the molecular fit, lizardite also features a perfect structure (in comparison to the corrugated antigorite), which is favourable to the method (II, Thomas and Midgleya 2004).

Paper I addresses a problem with mine tailings. The profitable advantages with already ground state of the tailings is diminished by the hazardous nature of the material. Their chemically processed nature implies that components that are added to the material may not influence the mineralogical outcome, but compromise the safety of the CCM-processing environment. There is no significant difference in the results between rocks and tailings produced from these rocks, with respect to production of $Mg(OH)_2$. However, if tailing material has gone through chemical processing, they may react in a violent manner when they are processed with the ammonium salt and the ammonium solution. The ore processing chemicals present in the tailings react with the ammonium solution even without direct contact, through the fumes, even after the material is washed with excessive amounts of distilled H_2O. Such a reaction does not occur with unprocessed host rocks, suggesting that the difference is related to the ore enrichment process. With other types of enrichment solvents or other processing chemicals the hazardous reaction may not occur, which enables exploitation of the tailing material as well (I, Gerdemann et al 2007). It is, thus, important to know what kind of chemical processing the tailings have gone through before they may be considered suitable or unsuitable for CCM.

5.2 Methodological observations

Extraction of Mg at a temperature of 480 °C produces better results than at 440 °C (I), in agreement with previous studies developing the method (Nduagu et al 2012b, Fagerlund et al 2010). The differences in results between the temperatures are significant and, therefore, the experiments in Papers II and III were only conducted at 480 °C.

The differences in theoretical amounts and actually produced $Mg(OH)_2$ are acknowledged in Paper I and further discussed in Papers II and III. Up to 97 wt% of the Mg ions found in the precipitation liquid are precipitated as $Mg(OH)_2$. However, most of the Mg in the raw material is not extracted from the rock material at all and is left in the insoluble material (Figure 9) (I). Thus, a large amount of Mg in the rock material is filtered out from the process and the fundamental problem of the method is traced to the extraction step and to the reactions between the material and the ammonium salt (I, II, III).

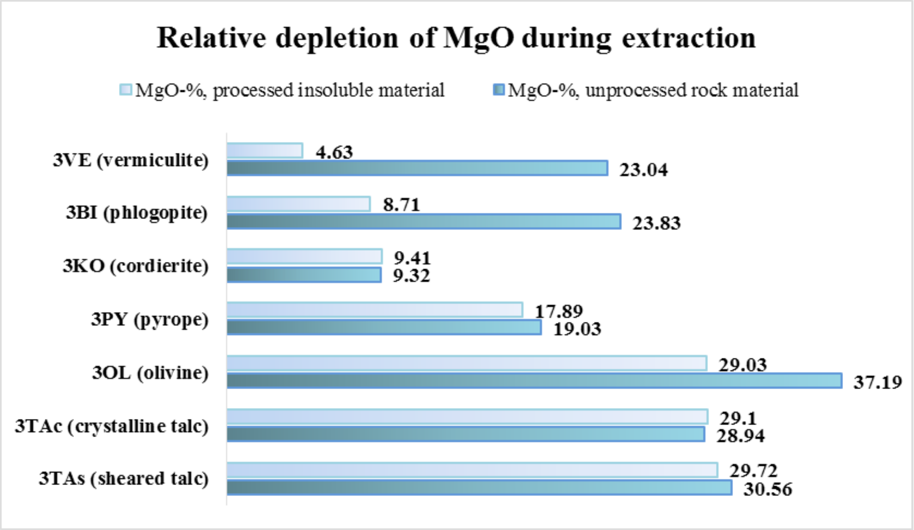


Figure 9. Depletion of MgO during the extraction process.

The pH-values for precipitation of the Fe (pH ~8) and Mg (pH ~11) in the process have been established by previous experiments (Nduagu et al 2012a, 2012b). However, the Fe ion from each sample is precipitated at slightly different pH (I, II, III). All Fe has to be removed before precipitation of Mg. Therefore individual and careful measuring and filtration is absolutely necessary (Nduagu et al 2012a, 2012b). Even though Mg is supposed to precipitate around pH ~11, some Mg does precipitate at lower pH together with Fe. A slow and stepwise increase of pH from pH ~1 to pH~8 is therefore advisable, with several filtration steps, in order to keep the Mg ions from precipitating together with Fe. For each sample, the precipitations of Mg and Fe overlap (I, II, III), but the overlapping range can be kept under control with precise execution.

Contamination and presence of Fe is addressed in Paper I. Even with careful precipitation, Fe-contamination during production of $Mg(OH)_2$ can occur, which is noted during both dry and wet carbonation. Precipitated and dried $Mg(OH)_2$ does not necessarily show any sign of Fe contamination, but during carbonation it turns slightly yellow or brown. This suggests that Fe is still present in the samples (Figure 10). This is a problem if the further use of the $MgCO_3$ requires a pure product. From the mineral carbonation point of view, it is not a problem because also FeO can bind CO_2, producing an iron carbonate, siderite ($FeCO_3$).

For "the ÅA route" Fe is mainly an inconvenience and an additional energy consumer for large-scale processing (Fagerlund 2012). However, if precipitating Fe requires several filterings, it may become a source of

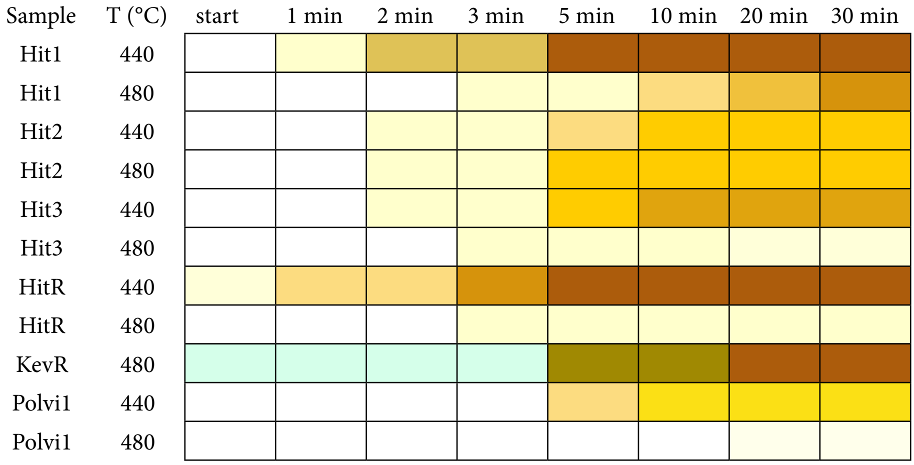


Figure 10. Colour change of the material during wet carbonation at T (°C) ~30 and 1 atm. The optimal result is seen in sample Polvi1, processed in 480 °C. The colours used in the chart present the exact colour/shade of the carbonation solution at a certain time point. For each appearing shade/colour change, a description of the colour was written down as well as a marking coloured with a matching crayon.

contamination or other errors (I). During experimentation (I, II, III), Fe tended to stick on glassware, which means that some Fe is removed during processing. This may affect measurements. In cases where Fe present in the precipitation needs to be minimized, a large part of Fe oxides and Fe hydroxides (hematite [Fe_2O_3], goethite [FeO(OH)]) can often be removed from the process already before the extraction. The grade of contamination can thus be reduced. Fe is readily removed from samples containing Fe in the form of magnetite (Fe_3O_4) by using a magnetic separator. For non-magnetic forms of Fe oxides/hydroxides, removal can be done through flotation if the host rock density and/or flotation properties differ enough from the Fe-phase present. Separation methods based on density are both easy and affordable.

Instrumental and material limitations create possible error sources for this thesis. If such has been a concern it is discussed respectively (I, II, III). The two main concerns are discussed especially in Paper III. In order to present how samples of Paper III performed in relation to each other, SEM-EDX was used to measure relative depletion of Mg in raw material before and after processing. For some samples, the results of depletion were negative. This suggests that SEM-EDX was an inadequate method. However, as the measurements were meant to be indicative and not to be used as exact data, they were published (III). The concern was addressed in discussion (III). Other types of measurements were not possible due to the second main problem, access to available material. Other experiments were repeated 2-3 times (I-III), but for pyrope and cordierite there was not enough material available in order to do more than one experiment. The long experimental history of the method (Fagerlund et al 2010, Nduagu et al 2012b, Romão 2015) and previous correlating reproducibility (I-III) supported the decision to include the samples and use the data in a similar manner as was done with the other samples.

6 Conclusions and suggestions for future work

As a result of studies executed in Papers I, II and III, the following conclusions may be drawn:

Mineralogical characteristics play a significant role in mineral carbonation processes. During this PhD-project, it has been found that the most profitable raw material for "the ÅA route" is a phyllosilicate-bearing rock originating from an un-metamorphosed phyllosilicate rock with high Mg and H_2O content, displaying a structure where Mg is easily accessible. In this case vermiculite formed by alteration of phlogopite. The other profitable material is a phyllosilicate formed by hydrothermal alteration of a nesosilicate-bearing peridotite. In this study, lizardite formed from dunite.

The results can confidently be utilised in future development work. Research considering the mineralogical studies brought the method closer to full-scale commissioning. Studies like the ones presented in this thesis are important in order to find effective methods battling the global warming.

Letting the mineralogical findings to move the study forward resulted in new and unexpected results. Each additional study area presented here was based on previous published results. The studies presented in Paper II were planned during production of Paper I, when it was noted that particular features in serpentinites influenced the results of the experiments. The results on serpentinites and serpentine minerals in Paper II were further developed in Paper III. The hypotheses were either overruled or confirmed through experiments and the central conclusions are listed below.

Also other factors than a high Mg content are important for a profitable outcome. A proper compositional percentage of magnesium was essential for positive results, as expected. The present crystalline H_2O was even more important to the successfulness of a sample. Some rocks with high Mg content produced less $Mg(OH)_2$ than samples with slightly lower Mg content that had more mineral-bound OH^-. However, it was noted that the presence of other features with positive effects balanced a lower H_2O. In most cases, a minimum of ~12 wt% crystalline H_2O is required for a profitable outcome. Another significant result is the accessibility to Mg in a mineral. Depending on the mineral structure and the position of Mg in the mineral lattice, the ammonium sulphate is either able or unable to break OH^-/O bonds holding the Mg in the structure. This influenced the extraction significantly.

Even though the metamorphic grade may not influence the actual processing, it does affect the production costs and energy consumption. During metamorphism, the mineral structure may change and the hypothesis was that it would influence the process. The result was unexpected and showed only a small extraction difference between similar rocks in different metamorphic grades. However, sample preparation is strongly influenced by the metamorphic grade of the raw material. Higher grade rocks required more energy and longer time in order to produce the necessary consistency.

The results presented here contribute especially to the mineralogical knowledge on serpentinites and serpentine minerals. The original hypothesis of serpentinites being suitable as raw materials for "the ÅA route" was not as straightforward as originally had been assumed. Based on the mineral structure, lizardite-bearing serpentinite rocks were found to be more promising than antigorite-bearing serpentinite rocks, yet the protoliths to the serpentinites have an even stronger influence on the outcome. Dunite samples produced better results than samples originating from other peridotites. A positive result gained in Paper I was that the timescale the serpentinite material is usable. Based on samples from zero exposure to weathering to samples exposed to weathering for 15 years in Finnish natural conditions [T (°C) from +30 to -25], it was concluded that weathering is irrelevant to the suitability of the serpentinite material.

A simple microscope study can give a hint whether a rock might be a suitable raw material. A microscope can reveal mineralogical characteristics that influence the mineral carbonation process. It is possible to detect if there are hydrous/Mg-rich minerals present and if the sample is pure or if it has contaminants/inclusions. Some textures reflect the protolith of a rock which is informative e.g. in serpentinite rocks.

Future work could involve:

- **Determining whether early removal of Fe increases profitability.** Precipitating Fe for carbonation (or other) purposes is a part of the "the ÅA route" process. As Fe tends to overlap precipitation of Mg, removing it before processing may be an alternative. Early removal of Fe may also make the processing of Mg easier and faster. This alternative would be best suited for rocks and minerals where Fe is found in magnetic form and/or as clearly concentrated areas. Such minerals are for example dunitic serpentinites, as serpentinisation of olivine produces magnetite.

- **A study focusing on the influence of metamorphic grade.** One important topic for future work is to see how the metamorphic grade of the raw material fits to the mineralogical flow chart. Low grade rocks are less dense and contain more H_2O than high grade rocks. For further development of "the ÅA route", it would be important to find out whether the metamorphic grade plays an essential role for the process and if so, what is the mechanism behind it. This unsolved question arose during the interpretation of the data in Paper III. Finding the answer is a natural next mineralogical step for the mineral carbonation study.

- **Finding out if tailings could be pre-treated in order to increase their suitability.** The results from serpentinite tailings are equal to those from serpentinite rocks, suggesting that processed ground tailings would be more advantageous than the unprocessed rocks. Unfortunately, chemicals originating from the ore enrichment processes caused violent, hazardous reactions and for this reason the tailings were deemed unsuitable for the CCM-process. Removal of these chemicals could make even tailings a possible raw material.

Several of the obstacles for "the ÅA route" related to the mineralogical properties of the raw material have been conquered, but further research on the influence of mineralogical features in mineral carbonation processes is necessary. Deeper knowledge about the essential characteristics will make future plants more profitable, as the process can be adjusted correctly and unsuitable material can be avoided.

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Appendix A

Basic geological and mineralogical information of the samples in Papers I-III.

Paper	Sample	Mine/location	Rock type/ mineral	Silicate group	MgO wt%	H_2O wt%
I	Hit1	Hitura, Finland	Serpentinite	Phyllosilicate	42.41	12.5
I	Hit2	Hitura, Finland	Serpentinite	Phyllosilicate	42.49	12.58
I	Hit3	Hitura, Finland	Serpentinite	Phyllosilicate	42.80	14.61
I	HitR	Hitura, Finland	Serpentinite tailing	Phyllosilicate	35.5	13.87
I	Kev1	Kevitsa, Finland	Pyroxenite	Inosilicate	19.38	1.52
I	KevR	Kevitsa, Finland	Pyroxenite tailing	Inosilicate	23.48	3.55
I	Pam1	Pampalo, Finland	Andesite tuff	Tectosilicate	4.44	7.25
I	Pam3	Pampalo, Finland	Iron formation	Phyllosilicate/ Inosilicate	2.62	0.44
I	Pam4	Pampalo, Finland	Chlorite-talc schist	Phyllosilicate	29.46	14.32
I	Polvi1	Mondo Minerals, Polvijärvi, Finland	Serpentinite	Phyllosilicate	45.19	12.61
II	AntN	Modum, Norway	Antigorite dominating serpentinite	Phyllosilicate	40.85	18.94
II	LizN	Modum, Norway	Lizardite dominating serpentinite	Phyllosilicate	41.12	19.73
II	AntF	Hitura, Finland	Antigorite seam	Phyllosilicate	37.80	12.51
II	LizIT	Elba, Italy	Lizardite	Phyllosilicate	39.59	13.84
II	SerpS	Piteå, Sweden	Serpentinite	Phyllosilicate	42.33	14.72
III	3TAc	Mondo Minerals, Polvijärvi, Finland	Crystalline talc	Phyllosilicate	23.31	11.2
III	3TAs	Mondo Minerals, Polvijärvi, Finland	Sheared talc	Phyllosilicate	25.44	7.68
III	3VE	Sokli, Finland	Vermiculite	Phyllosilicate	21.85	15.34
III	3BI	Skräbböle, Finland	Biotite (phlogopite)	Phyllosilicate	27.39	1.1
III	3OL	Åheim, Norway	Olivine (forsterite)	Nesosilicate	46.30	0.58
III	3PY	Podsedice, Czech Republic	Garnet (pyrope)	Nesosilicate	21.87	0.14
III	3KO	Kiuruvesi, Finland	Cordierite	Cyclosilicate	9.42	1.63

Appendix B

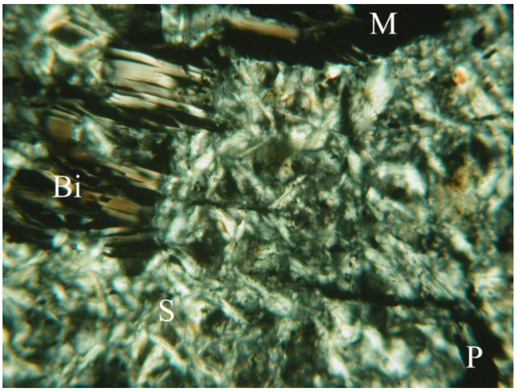
The bulk composition of the samples in Papers I-III (analyses marked with an asterisk (*) are normalized to 100 wt%).

	Hit1	Hit2	Hit3	HitR	Kev1*	KevR*	Pam1*	Pam3*	Pam4	Polvi1	AntN
SiO_2	33.97	34.39	30.53	32.36	50.01	45.35	38.53	59.55	41.70	39.02	35.51
TiO_2	0.02	0.02	0.02	0.05	0.45	0.33	1.94	0.33	0.28	0.05	0.01
Al_2O_3	0.00	0.00	0.00	1.09	4.13	3.17	12.47	12.47	5.47	2.33	0.26
FeO	11.50	10.79	11.96	11.14	6.62	8.05	12.57	16.08	5.84	4.04	2.34
MnO	0.15	0.13	0.14	0.19	0.22	0.21	0.42	0.08	0.18	0.06	0.02
MgO	42.41	42.49	42.8	40.77	19.38	23.48	4.44	2.62	27.85	44.14	40.85
CaO	0.12	0.06	0.2	0.42	17.04	14.97	14.33	4.48	4.94	0.04	1.12
K_2O	0.00	0.00	0.01	0.2	0.43	0.19	5.71	3.89	0.02	0.00	0.36
Na_2O	0.21	0.26	0.27	0.2	0.00	0.15	1.91	0.00	0.00	0.22	0.00
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.07	0.00	0.00	0.44
CrO	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00
S	0.11	0.11	0.78	0.94	0.20	0.54	0.27	0.00	0.00	0.05	0.01
LOI	12.5	12.6	14.61	13.87	1.52	3.55	7.24	0.44	14.32	12.61	18.94
Tot.	100.99	100.83	101.33	101.23	100.00	100.00	100.01	100.01	100.6	102.56	99.88

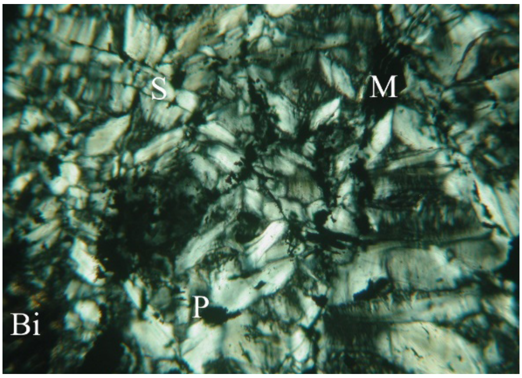
	LizN	AntF	LizIT*	SerpS*	3TAc	3TAs	3VE	3BI	3OL*	3PY	3KO
SiO_2	34.66	44.50	39.25	35.73	62.45	64.69	36.63	43.62	42.21	39.13	49.85
TiO_2	0.01	0.00	0.01	0.01	0.02	0.02	0.56	0.14	0.00	0.42	0.20
Al_2O_3	0.26	0.00	2.87	0.13	0.35	0.30	11.25	12.35	0.62	21.86	30.46
FeO	2.28	5.11	4.20	6.70	2.65	1.41	8.73	3.43	9.05	9.42	8.06
MnO	0.02	0.00	0.03	0.12	0.00	0.00	0.11	0.04	0.09	0.35	0.33
MgO	41.12	37.80	39.59	42.33	23.31	25.44	21.85	27.39	46.30	21.87	9.42
CaO	1.09	0.00	0.14	0.07	0.03	0.13	4.64	0.45	0.06	4.24	0.10
K_2O	0.28	0.00	0.05	0.08	0.01	0.00	0.80	10.07	0.12	0.01	0.10
Na_2O	0.00	0.00	N/A	0.01	0.00	0.26	0.00	0.12	0.96	0.00	0.00
P_2O_5	0.42	0.00	N/A	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00
CrO	0.00	0.00	0.01	0.08	0.00	0.00	0.00	0.00	0.00	2.43	0.00
S	0.00	0.00	N/A	N/A	0.01	N/A	N/A	N/A	N/A	N/A	N/A
LOI	19.73	12.51	13.84	14.72	11.02	7.68	15.34	1.10	0.58	0.14	1.63
Tot.	99.88	99.91	100.00	99.99	99.84	99.94	100.00	98.70	100.00	99.88	100.16

Appendix C

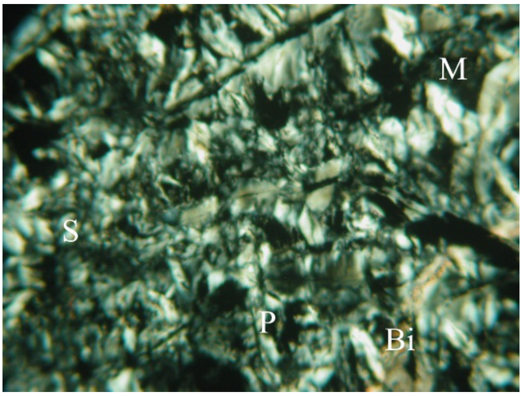
Mineralogical sample descriptions (Papers I-III).



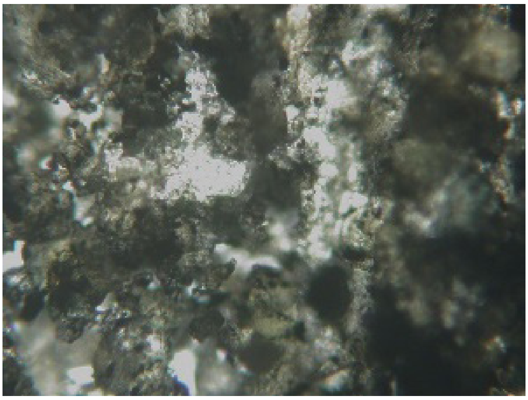
Serpentinite Hit1 (Transmitted cross-polarised light). Sample rock has metamorphosed in greenschist facies. It is an even-grained rock with magnetite (Fe_3O_4) (M) and pyrite (FeS_2) (P) veins (ø 0.5–2 mm). 90 % of the sample consists of serpentinite (S), 5 % of magnetite and pyrite and 5 % of subhedral biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) (Bi) /opaques.



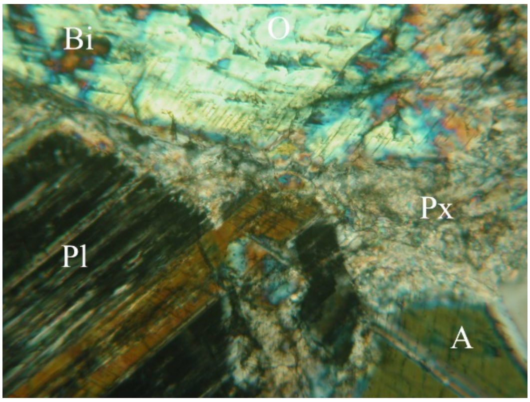
Serpentinite Hit2 (Transmitted cross-polarised light). Sample rock has metamorphosed in greenschist facies. It is an even-grained rock with magnetite (Fe_3O_4) (M) and pyrite (FeS_2) (P) veins (ø 0.5–2 mm). 90 % of the sample consists of serpentinite (S), 5 % of magnetite and pyrite and 5 % of subhedral biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) (Bi) /opaques.



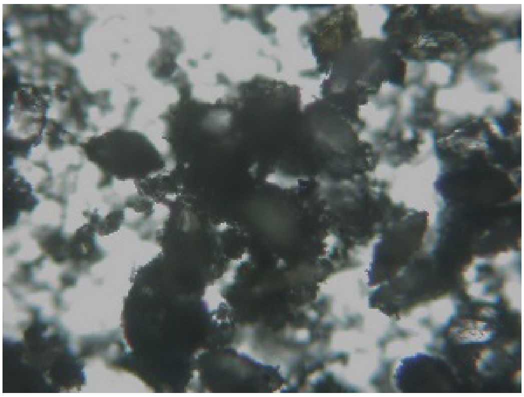
Serpentinite Hit3 (Transmitted cross-polarised light). Sample rock has metamorphosed in greenschist facies. It is an even-grained rock with magnetite (Fe_3O_4) (M) and pyrite (FeS_2) (P) veins (ø 0.5–2 mm). 90 % of the sample consists of serpentinite (S), 5 % of magnetite and pyrite and 5 % of subhedral biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) (Bi) /opaques.



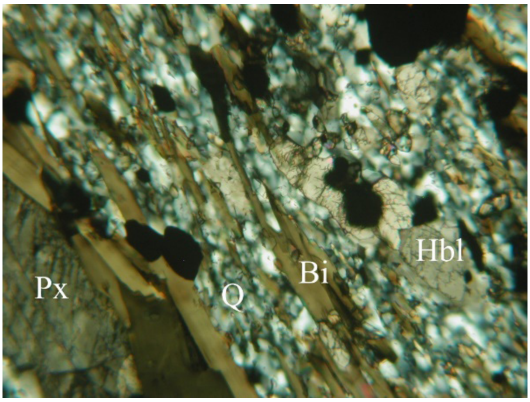
Serpentinite tailing HitR (Transmitted cross-polarised light). HitR has been produced from rock material comparable to samples Hit1-3. It has been depleted in ore metals through selective flotation.



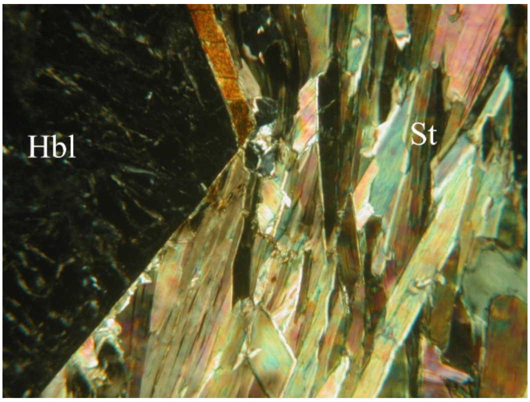
Pyroxenite Kev1 (Transmitted cross-polarised light). Sample rock is a dark green fine-grained pyroxenite with occasional smaller grains (ø 1–2 mm). It consists mostly of pyroxenes (NaCa)(Mg,Fe,Al)(Al,Si)$_2$O$_6$ (Px) and amphiboles (NaCa$_2$(Mg,Fe,Al)$_5$(Al,Si)$_8$O$_{22}$(OH)$_2$ (A) (< 80 %). Secondary minerals are biotite (K(Mg,Fe)$_3$AlSi$_3$O$_{10}$(F,OH)$_2$) (Bi), plagioclase ((Na,Ca)(Si,Al)$_4$O$_8$), (Pl), iron oxides (Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$) and olivine (O) (Fe,Mg)2SiO4).



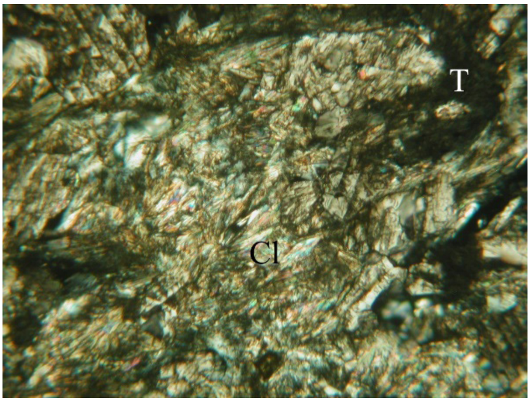
Pyroxenite tailing KevR (Transmitted cross-polarised light). KevR has been produced from rock material comparable to sample Kev1. It has been depleted in ore metals through selective flotation.



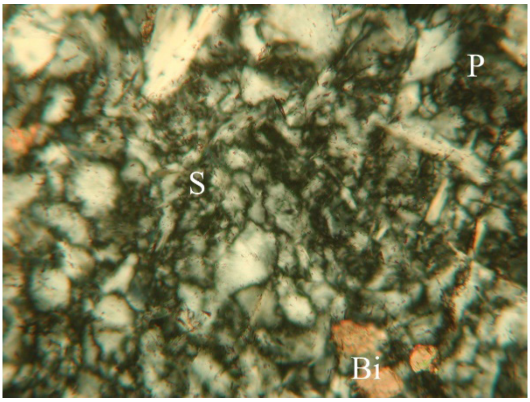
Andesite tuff Pam1 (Transmitted cross-polarised light). Sample has porphyritic texture. Matrix consists of quartz SiO_2 (Q), hornblende ($(Ca,Na)_{2-3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$) (Hbl) and biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) (Bi) while porphyries consist of plagioclase ($(Na,Ca)(Si,Al)_4O_8$), clino- ($(Ca,Mg,Fe,Na)(Mg,Fe,Al)(Si,Al)_2O_6$) and ortopyroxenes ($(Mg,Fe,Ca)(Mg,Fe,Al)(Si,Al)_2O_6$) (Px).



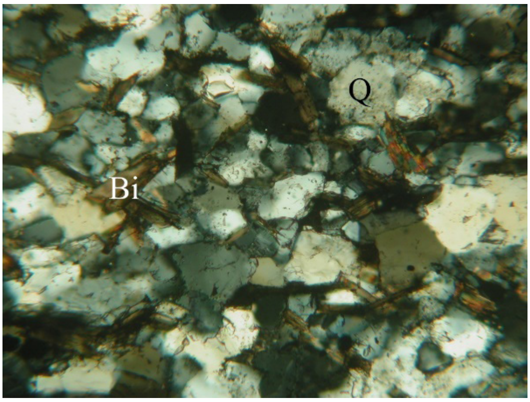
Iron formation Pam3 (Transmitted cross-polarised light). Sample rock is a strongly migmatized iron formation with well-developed lineation. It is fine- to medium-grained with occasional talc ($Mg_3Si_4O_{10}(OH)_2$) veins.
Primary minerals are stilpnomelane ($K(Fe^{2+},Mg,Fe^{3+})_8(Si,Al)_{12}(O,OH)_{27}\cdot n(H_2O)$) (St) and hornblende ($(Ca,Na)_{2-3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$) (Hbl).



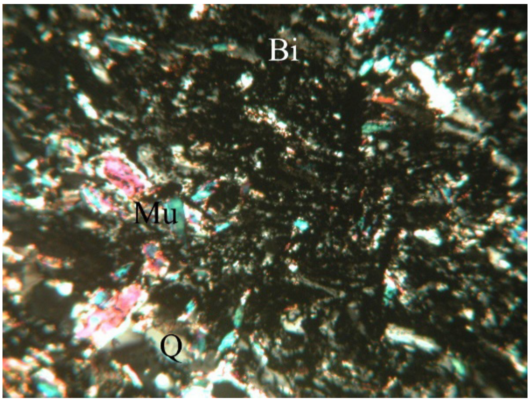
Chlorite-talc schist Pam4 (Transmitted cross-polarised light). Sample rock is a chlorite-talc schist (chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2\cdot(Mg,Fe)_3(OH)_6$) (Cl), talc ($Mg_3Si_4O_{10}(OH)_2$) (T)) with light chlorite green colour. ~50 % consist of talc, ~45 % of chlorite and ~5 % of pyrite (FeS_2), magnesite ($MgCO_3$) and opaques.



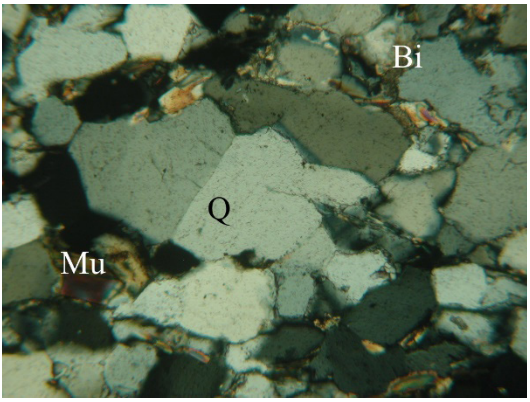
Serpentinite Polvi1 (Transmitted cross-polarised light). Sample rock has metamorphosed in greenschist facies. It is an evengrained rock with magnetite (Fe_3O_4) and pyrite (FeS_2) (P) veins (ø 0.5–2 mm). 90 % of the sample consists of serpentinite (S), 5 % of magnetite and pyrite and 5 % of subhedral biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) (Bi) /opaques. Small naturally occurring carbonates are also present.



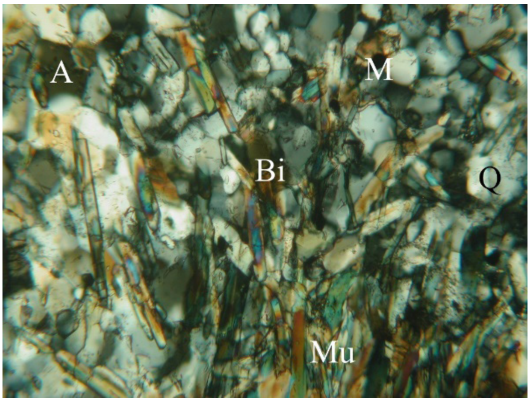
Mica schist Talvi1 (Transmitted cross-polarised light). Sample rock is a fine-grained mica schist that consists mainly of quartz (SiO_2) (Q) and plagioclase ($(Na,Ca)(Si,Al)_4O_8$), with biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) (Bi) and ilmenite ($FeTiO_3$) as secondary minerals.



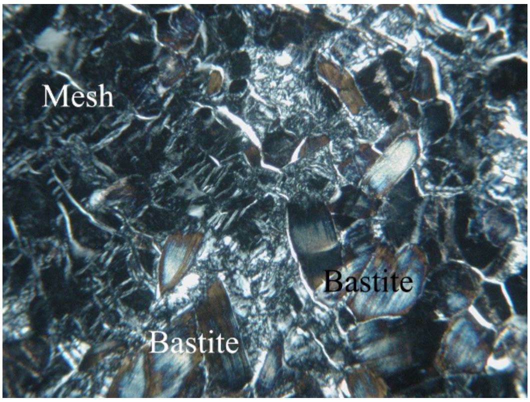
Black schist Talvi2 (Transmitted cross-polarised light). Sample rock is a very fine-grained black schist with banded sills of pyrite (FeS_2). Primary minerals are quartz (SiO_2) (Q) and biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) (Bi). Secondary minerals are pyrite, muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) (Mu) and plagioclase ($(Na,Ca)(Si,Al)_4O_8$).



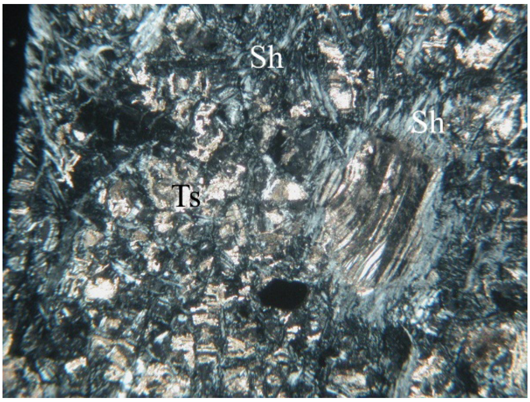
Quarzite Talvi3 (Transmitted cross-polarised light). Sample rock is a quartzite with fine- to medium-sized evenly distributed grains. It consists of quartz (SiO_2) (Q) with biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) (Bi) and muscovite (Mu) ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) as secondary minerals.



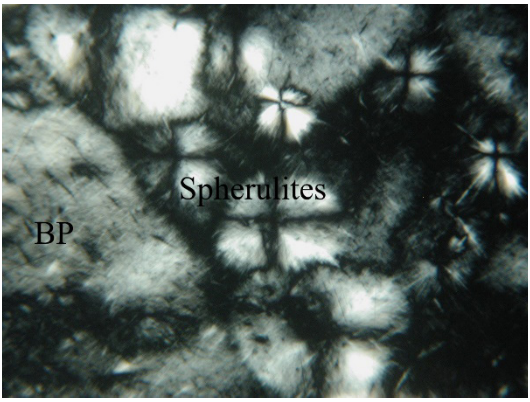
Mafic vulcanite Pam2 (Transmitted cross-polarised light). Sample rock is a foliated porphyritic fine-grained mafic volcanite. Primary minerals are amphibole ($NaCa_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$ (A) and plagioclase ($(Na,Ca)(Si,Al)_4O_8$) (~70 %). Secondary minerals are biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) (Bi), muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) (Mu), quartz ($SiO_2$) (Q), magnetite ($Fe_3O_4$) (M) and opaques.



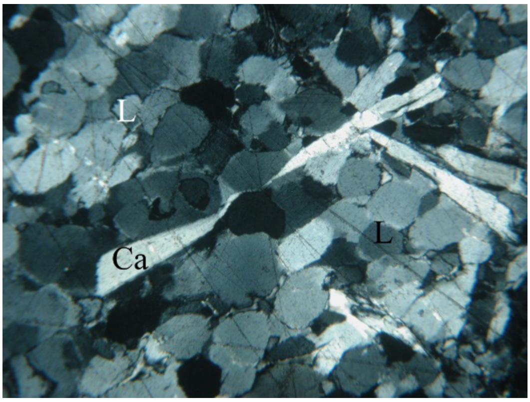
Norwegian antigorite-dominating serpentinite AntN (Transmitted cross-polarised light). Sample rock is collected from the Modum area in Norway and displays a bright green colour with cloudy surface. It contains 48.57 % of MgO. Sample is dominated by a mesh (Mesh) textured serpentinite and accompanied by talcy serpentinite grains and stained talc ($Mg_3Si_4O_{10}(OH)_2$). Bastite (Bastite) grains are found as groups in the middle parts of the sample.



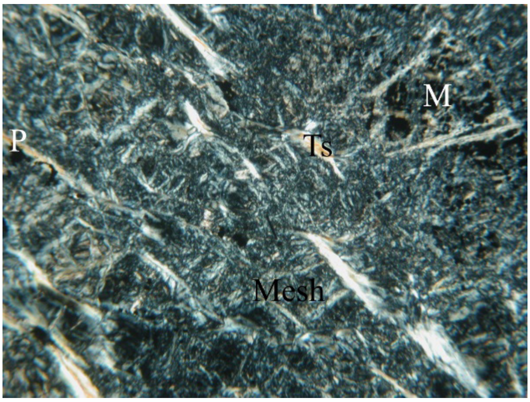
Norwegian lizardite-dominating serpentinite LizN (Transmitted cross-polarised light). Sample rock is collected from the Modum area in Norway. It displays a light yellow colour and fine-grained texture. It contains 49.30 % of MgO. Some mesh texture is present but > 50 % of the sample consists of a sheafy (Sh) texture. Such texture is usually present in the original form of the parent rock altered into serpentinite. Stained talc ($Mg_3Si_4O_{10}(OH)_2$) (Ts) is also present.



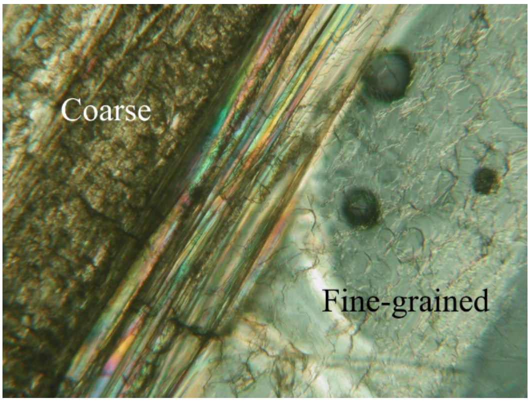
Hitura antigorite seam AntF (Transmitted cross-polarised light). Sample rock is a seam collected from the Hitura mine from a serpentinite gangue pile. It displays a dark green colour and the columnar structure is clearly visible. It contains 42.14 % of MgO. Mesh texture, spherulites (Spherulites) and blurred pseudomorphs (BP) after olivine dominate the sample. Talcy serpentinite and stained talc ($Mg_3Si_4O_{10}(OH)_2$) are also present. Some opaque minerals (pyrite, FeS_2) are found.



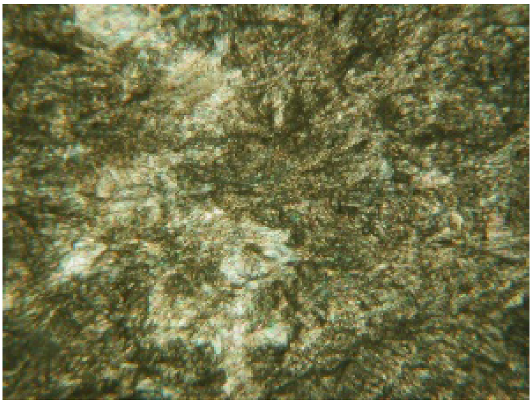
Elba lizardite LizIT (Transmitted cross-polarised light). Sample rock is collected from the Elba island in Italy. It displays a blue-green fine-grained texture with calcite ($CaCO_3$) veins (Ca) and bright green flakes in contacts. A slickenside texture on the rock sample is visible. It contains 39.10 % of MgO. Over 90 % of the sample consists of rounded lizardite $Mg_3Si_2O_5(OH)_4$ grains (L). Some stained talc ($Mg_3Si_4O_{10}(OH)_2$) is present and sheafs of antigorite ($(Mg,Fe)_3Si_2O_5(OH)_4$) is visible.



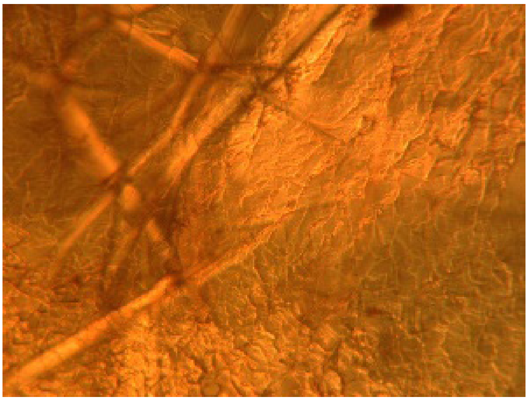
Swedish high-H_2O serpentinite SerpS (Transmitted cross-polarised light). Sample rock is collected from Piteå in Sweden. It displays a regular serpentinite rock with dark moldy green colour, light veins and magnetite (Fe_3O_4) (M) and pyrite (FeS_2) (P) grains. Traces of nickel (Ni) and cobalt (Co) appear regularly during the mineralogical measurements. The sample contains 40.63 % of MgO. The sample consists mostly of mesh (Mesh) texture together with stained talc ($Mg_3Si_4O_{10}(OH)_2$) (Ts). Some opaque minerals (magnetite (Fe_3O_4), pyrite (FeS_2)) are evenly distributed in the sample.



Crystalline talc 3TAc (Transmitted cross-polarised light). Sample mineral is a crystalline talc ($Mg_3Si_4O_{10}(OH)_2$) vein that consists of 97.5 % talc and 2.5 % pyrite (FeS_2). It contains 23.31 wt% MgO and 11.02 wt% crystalline H_2O. The colour of the bulk sample is very light green with pearly luster. The sample is coarse-grained with a massive fibrous crystal structure. Both fine-grained and coarse-grained areas are found. Coarse-grained areas have a scaly texture.

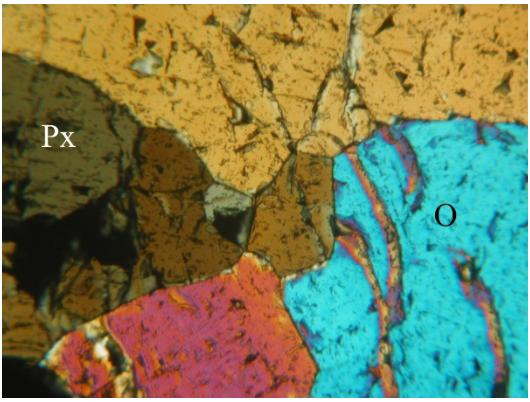


Sheared talc 3TAs (Transmitted cross-polarised light). Sample mineral is a sheared talc vein that consists of 98.5 % talc ($Mg_3Si_4O_{10}(OH)_2$) and 1.5 % pyrite (FeS_2). It contains 25.44 wt% MgO and 7.68 wt% crystalline H_2O. The colour of the bulk sample is light blue-green and has a waxy luster. The sample represents fine-grained and medium-grained areas, which differ from each other only by the grain size.



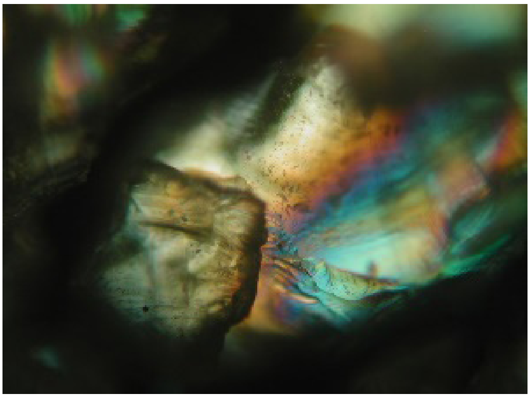
Vermiculite 3VE (Transmitted cross-polarised light). Sample mineral is a vermiculite ($(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2$) consisting of 95 % vermiculite and 5 % talc ($Mg_3Si_4O_{10}(OH)_2$). It contains 21.85 wt% MgO and 15.34 wt% crystalline H_2O. The ~5 % calcite ($CaCO_3$) detected is found in the interlayer between the T-O-T sheets.

Phlogopite 3BI (Transmitted cross-polarised light). Sample mineral is a very pure phlogopite, ($K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,F)_2$). It contains 27.39 wt% MgO and 1.10 wt% crystalline H_2O.



Forsteritic olivine 3OL (Transmitted cross-polarised light). Sample rock consists of 90 % forsterite rich olivine ($(Fe,Mg)_2SiO_4$), (O), 5 % pyroxenes $(NaCa)(Mg,Fe,Al)(Al,Si)_2O_6$ (Px) and 5 % chromium(IV)oxide (CrO_2) and traces of magnesite ($MgCO_3$). The sample contains 46.30 wt% MgO and 0.58 wt% crystalline H_2O. The rock is fine grained, light green with some large (∅ ~2-3 cm) emerald green olivine crystals (~10 %).

Pyrope garnet 3PY (Stereomicroscope transmitted/incident light illumination). Sample mineral consists of a Mg-rich garnet (82.65 % pyrope ($Mg_3Al_2(SiO_4)_3$), 8.76 % grossular ($Ca_3Al_2(SiO_4)_3$), 5.08 % almandine ($Fe_3Al_2(SiO_4)_3$), 2.0 % andradite ($Ca_3Fe_2(SiO_4)_3$), 0.75 % spessartine ($Mn_3Al_2(SiO_4)_3$) and 0.65 % uvarovite ($Ca_3Cr_2(SiO_4)_3$)). Sample has no detectable inclusions or contaminants. It contains 21.87 wt% MgO and 0.14 wt% crystalline H_2O.



Cordierite 3KO (Stereomicroscope transmitted/incident light illumination). Sample mineral is a cordierite ($(Mg,Fe)_2Al_3(Si_5AlO_{18})$) with 5 % of impurities such as pyrite (FeS_2), biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) and zircon ($ZrSiO_4$). It contains 9.42 wt% MgO and 1.63 wt% crystalline H_2O.

Errata

In Paper I "Suitability of Finnish mine waste (rocks and tailings) for Mineral Carbonation", inaccurate values for Figure 2 are published. The correct values are found in the material description of this thesis as well as in Paper II "the Significance of the Serpentinite Characteristics in Mineral Carbonation by "the ÅA route" for the sample "HITR".

Due to the error, the actual value for the required minimum of crystalline H_2O (> 2.5 wt%) in Paper I, is factually > 12.5 wt%.

Incorrect values as published in "Proceedings of Ecos 2014":

Sample	**HIT3**	**PAM4**	**HIT2**	**POLVI1**	**HIT1**	**HITR**	**PAM1**	**KEVR**	**KEV1**	**PAM3**
H_2O wt%	3.29	3.13	2.75	2.63	2.58	2.55	1.34	0.79	0.33	0.10

Correct values:

Sample	**HIT3**	**PAM4**	**HIT2**	**POLVI1**	**HIT1**	**HITR**	**PAM1**	**KEVR**	**KEV1**	**PAM3**
H_2O wt%	14.61	14.32	12.60	12.61	12.50	13.87	7.24	3.55	1.52	0.44

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