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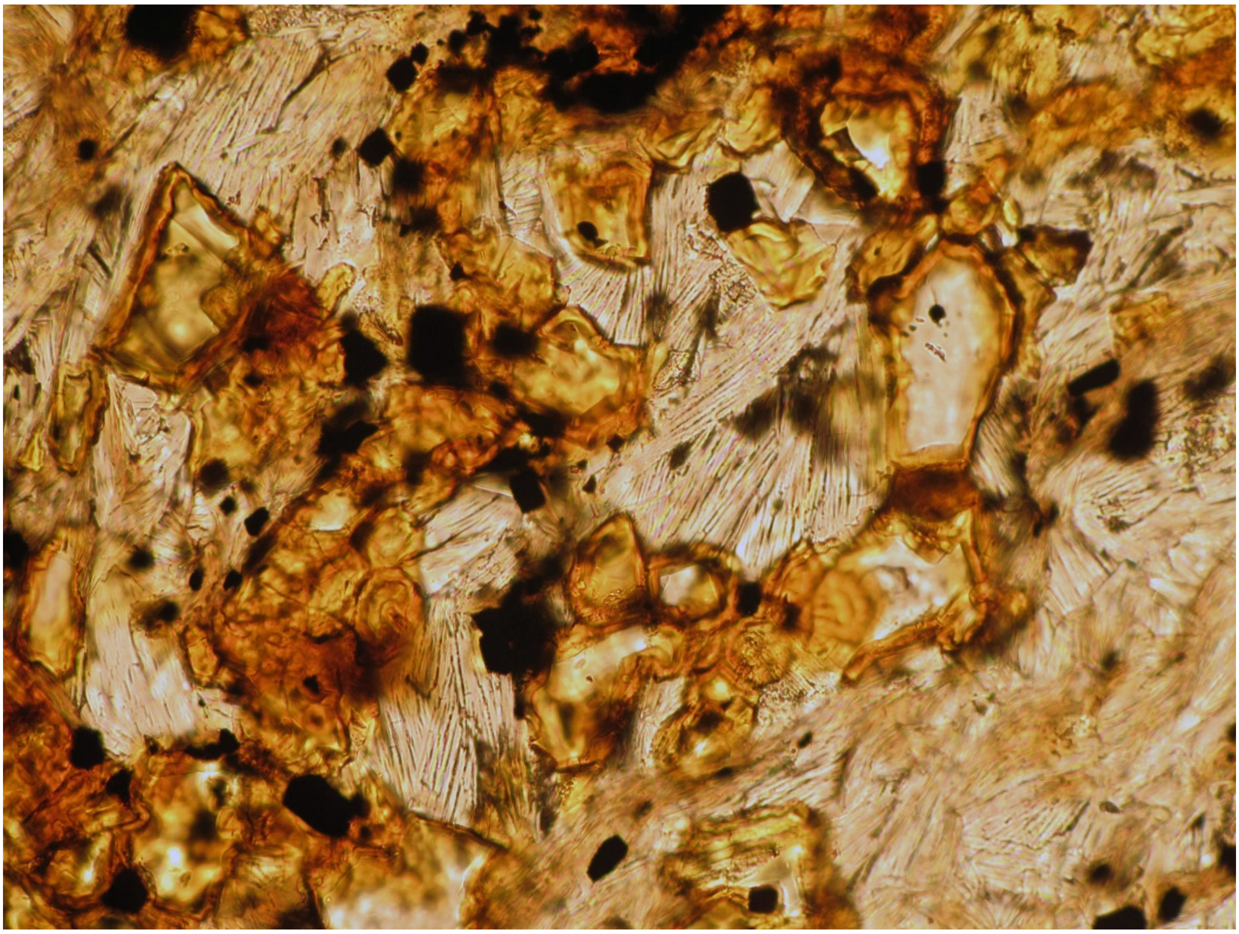

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Cover Figure:

Micrograph of the fireplace sopstone at the depth of 3 cm from the fire camber surface. Rims of the magnesite grains are decomposed to redbrown ferropericlase whereas talk flakes have remained intact. Length of the image is 0.33 mm.

DIVERSITY OF SOAPSTONES: CLASSIFICATION AND THERMAL BEHAVIOR

ANNE HUHTA

Academic dissertation to be presented with the assent of the Doctoral Training Committee of Technology and Natural Sciences of the University of Oulu for public defense in Auditorium IT 115, Linnanmaa, on March 22nd 2019, at 12 noon

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Diversity of soapstones: Classification and thermal behavior

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ABSTRACT

In the past, very little effort has been made to acknowledge large number of compositional and structural variations in rocks that are included in the group generally known as “soapstones”. Some of these variations have been proved not solely to sustain extremely well high temperature cycles in similar and more arduous thermal conditions than in fire chambers and in funnels, but to go through thermally induced changes which make the structure and composition of the rocks even harder.

The aim of this study was to create classification and nomenclature system to soapstones and to investigate what are the attributes that effect on the thermal shock resistance of carbonate soapstone (more closely magnesite soapstone), one of the classes in soapstone classification. In addition, an essential goal was to examine how the mineral composition and microstructure of carbonate soapstone alters due the use as fire chamber construction material over time.

Soapstones have an extensive range of variation in mineral composition. The current naming policy is insufficient, since the term “soapstone” describes poorly the major mineral composition in the rock. Hence, the definition, nomenclature and classification scheme for soapstones was developed based on the absolute and relative mineral compositions: Soapstone must contain 35– 75 vol.% talc, but not more than 35 % hard silicates (e.g. serpentine, amphibole). Although in some cases serpentine can be as soft as chlorite, it is here considered as a hard silicate from technical point of view. Serpentine-rich sections have to be removed by blasting instead of sawing as soapstones. Further division is based on oxide, chlorite and carbonate ratios. In addition, if the content of additional hard silicate exceeds 5 %, the silicate name is placed as a prefix.

To gain information about thermal durability of magnesite soapstones, the new test method for thermal shock resistance (TSR-test) was developed. The Electron Probe Microanalysis (EPMA) and the Field Emission Scanning Electron Microscopy (FESEM) were used to determinate the microstructures and chemical compositions of the magnesite soapstones. Soapstones having secondary planar foliation and more specifically, the presence of short cleavage domains with a rough form of planarity, yielded the highest thermal shock resistance.

The mineralogical changes causing hardening of the surface of the soapstones that have been subjected in to the fire chamber conditions over time were studied. The results show the following main reasons for the surface hardening: 1) Iron enrichment near the surface, particularly in the ferropericlase pseudomorph aggregates; 2) Brucite formation and further serpentinization; 3) talc-rim alteration to enstatite and/or forsterite; 3) Chlorite alteration to

anhydrate-chlorite phase. Furthermore, wood combustion gases participated surprisingly efficiently during the hardening process by Zn and K additions.

Recognizing the diversity of soapstone types and understanding the effects of the different structural and compositional forms on the thermal properties of these different rock types, enables soapstone industry to exploit the soapstone type having the best thermal durability. Hence, higher temperatures can be employed in fire chambers and in funnels, resulting more efficient and more environmentally friendly fireplaces due to more particulate-free combustion. The thesis also reveals the advantageous changes in mineralogy and in structure of soapstones used in high temperature environments. In addition, the new classification and nomenclature scheme of soapstones has also geological importance, since despite their wide structural and compositional variations, geological classification of soapstones did not exist.

TIIVISTELMÄ

Yleisesti vuolukiviksi kutsutaan mineraalikoostumukseltaan ja rakenteeltaan erilaisia kiviä, joita yhdistää suurehko talkkipitoisuus, vuoltavuus, sekä niiden käyttö lämpörasituksen kestoa vaativissa kohteissa. Tässä väitöskirjassa todetaan, että vuolukivilajeja on useita, ja että jotkin näistä kivilajeista kestävät erittäin hyvin termisen sokin aiheuttamaa rasitusta. Tämän lisäksi säännöllisesti käytössä olevan tulipesän ja savukanavien olosuhteet aiheuttavat magnesiittivuolukiven pinnan mineraalikoostumuksessa ja rakenteessa muutoksia, jotka ajan myötä kovettavat kiveä entisestään.

Tämän väitöskirjan päämäärinä olivat vuolukivien luokittelu- ja nimeämiskäytännön luominen, ja kivessä esiintyvien termisen sokin kestävyyteen vaikuttavien ominaisuuksien spesifioiminen. Lisäksi tavoitteena oli määrittää ne mineralogiset muutokset, jotka aiheuttavat tulipesän ja savukanavien olosuhteille altistuneen magnesiittivuolukiven pinnan kovenemisen ajan saatossa.

Vuolukivilajien mineraalikoostumus voi vaihdella suuresti. Nykyisin käytössä oleva nimi ”vuolukivi” kertoo lähinnä sen, että kivi on riittävän pehmeää, jotta sitä voidaan työstää käsin. Termi ei kuvaa kivessä esiintyviä päämineraaliseurueita. Tästä johtuen nähtiin aiheelliseksi kehittää vuolukivilajien absoluuttiseen sekä suhteelliseen mineraalikoostumukseen perustuvat määrittely-, nimeämis- ja luokittelukäytännöt, joiden mukaan vuolukiveksi voidaan kutsua kiveä, joka sisältää talkkia 35–70%, mutta kovien silikaattien määrä ei saa ylittää 35% (esim. serpentiini ja amfiboli). Tarkempi luokittelu perustuu oksidien, kloriitin ja karbonaatin suhteisiin. Mikäli kovien silikaatin määrä ylittää 5%, lisätään silikaatin nimi etuliitteeksi vuolukivilajin nimeen.

Väitöskirjan yhteydessä kehitettiin uusi testausmenetelmä, jolla voidaan tutkia erilaisten luonnonkivien termisen sokin kestävyyttä (TSR-testi). Testiä käytettiin apuna tutkittaessa makroskooppisesti samankaltaisten magnesiittivuolukivien termisen sokin kestoon vaikuttavia parametrejä. Näytteiden mikrorakenteet sekä mineraalikoostumukset määritettiin mikroanalysaattorilla (EPMA) sekä kenttäpyyhkäisyelektronimikroskoopilla (FESEM). Tulokset osoittivat niiden magnesiittivuolukivien kestävän parhaiten suuria lämpötilavaihteluita, joiden mikrorakenne koostuu ns. välitilaisesta foliaatiosta (spaced

foliation). Termisen sokin kestävyyden kannalta erityisen tärkeää oli välitilaisen foliaation folioituneiden saumojen lyhyys sekä epätasainen muoto.

Lisäksi väitöskirjassa on tutkittu tulipesän seinämien pinnassa ajan saatossa tapahtuneita mineralogisia muutoksia. Magnesiittivuolukiven pinta kovettuu tulipesässä pääasiassa seuraavista syistä: raudan rikastuminen pinnan läheisyyteen, erityisesti ferroperiklaasi-aggregaatteihin, brusiitin muodostuminen ja edelleen serpentiiniytyminen, talkkirakeiden reunojen muuttuminen enstatiitiksi ja/tai forsteriitiksi ja kloriitin muuttuminen vesiköyhäksi kloriittifaasiksi. Puun poltosta aiheutuneet palokaasut ovat osallistuneet prosessiin yllättävän tehokkaasti aiheuttaen sinkin ja kaliumin rikastumista magnesiittivuolukiven pintaan.

Ottamalla huomioon vuolukivilajien suuren määrän ja ymmärtämällä niissä esiintyvien rakenteiden ja kemiallisten koostumusten vaikutukset kunkin vuolukivilajin termisiin ominaisuuksiin, voidaan tulisijan kuumimpien osien rakennusmateriaaliksi valita kestävin vuolukivilaji. Tulipesän lämpötilaa voidaan näin nostaa erittäin korkeaksi, jolloin tuloksena on ympäristöystävällisempi, entistä vähemmän pienhiukkasia tuottava sekä polttopuuta kuluttava tulisija. Väitöskirja tuo ilmi tulipesän rakennusmateriaalina toimineen magnesiittivuolukiven pinnan rakenteessa ja mineralogiassa tapahtuneet hyödylliset muutokset. Lisäksi uusi vuolukivien luokittelu- ja nimeämiskäytäntö on merkittävä myös geologisesta näkökulmasta, sillä huolimatta vuolukivien laajasta rakenteellisesta ja koostumuksellisesta variaatiosta yhdenmukaista vuolukivilajien luokittelua ei ole aikaisemmin kehitetty.

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I wish to address my gratitude to Associate Professor Tonci Balic-Zunic from University of Copenhagen, whose expertise in XRD-analyzing was truly needed. Also, the help of Markku Leinos from Confederation of Finnish Construction Industries (RT) was invaluable during the early stages of this thesis. I want to express my gratitude to Juhani Lehikoinen (Chairman of the board) and Johannes Uusitalo (CEO) from Nunnanlahden Uuni Oy. Many fruitful discussions there during the years have taught me greatly about soapstone industry and gave me insight of applied significance of my studies. I would like to thank Sari Forss (OMS) for the excellent quality thin sections and Leena Palmu (Center of Microscopy and Nanotechnology, University of Oulu) for the help during many sessions with microprobe.

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I wish to express my gratitude to my PhD-student colleagues and my friends over two decades. Many challenges have been conquered (or deleted) with your help and support. Finally, I am grateful to my husband Jukkis, who has shared his knowledge and support with our journey together as colleagues and as a family with our children, Veera and Sakari.

Oulu, October 2018

Anne Huhta

ORIGINAL PUBLICATIONS AND AUTHOR'S CONTRIBUTION

This dissertation is based on the following three peer-reviewed articles:

Paper I Huhta, A. & Kärki, A., 2018. A proposal for the definition, nomenclature, and classification of soapstones. GFF 140(1), 38-43. https://doi.org/10.1080/11035897.2018.1432681

Paper II Huhta, A., Kärki, A. & Hanski, E., 2016. A new method for testing thermal shock resistance properties of soapstone – Effects of microstructures and mineralogical variables. Bulletin of the Geological Society of Finland 88, 21–46. https://doi.org/10.17741/bgsf/88.1.002

Paper III Huhta, A., Tuisku, P., Zunic, T-B. & Kärki, A., (in press) Magnesite soapstone in use of fire chamber constructions: Composition adaptation. Bulletin of the Geological Society of Finland.

Anne Huhta is the corresponding author in all the three published research articles. Her contribution to writing was 90% in papers I and II, and 85% in the paper III. The outcrop samples, drill cores and the samples from abroad studied in paper I and II were collected during "Sustainable Use of Soapstones"- research projects (VUKEI and VUKEII OY), where the author worked as a research assistant and later as a senior researcher. More information about contributions related to VUKE-projects can be found in the Introduction-chapter of this thesis. The magnesite soapstone samples studied in paper III were received from fireplace that has functioned as residential wood burning use in private home over 60 years. The soapstone classification and nomenclature scheme were re-developed by the author. In addition to hundreds of test cycles during the VUKEII-project the preliminary thermal shock resistance test was confirmed by final test runs and finished to its status by the author. Anne Huhta is also responsible for all the geochemical data obtained in this thesis except for the XRD-results in the paper III, which were carried out by Tonci Balic-Zunic from the University of Copenhagen. Data interpretations were performed by Anne Huhta with the help of co-authors. Pekka Tuisku contributed the pseudobinary models in paper III.

CONTENTS

1. INTRODUCTION

1.1 Background

The tentative soapstone classification scheme was first developed in the VUKE I-project. For that, the sample material was collected by hammer and mini diamond drill from domestic sites (197 pcs.), from diamond drill cores (206 pcs.) and from foreign sites. The sample acquisition was done by research assistants Tuomas Havela, Anne Huhta, Eemeli Rantala and Annika Vehviläinen and by geologists Mauri Niemelä, Seppo Leinonen, Heikki Pirinen, and technician Pentti Toivanen. Drill core studies were performed from drill cores of GSF by research assistants Tuomas Havela, Anne Huhta and Jani Kainulainen and the geologists Seppo Leinonen and Heikki Pirinen. The foreign acquisition was carried out in collaboration with the GSF and the University of Oulu by approaching foreign research institutes and operators of soapstone industry with a request to provide sample material for scientific use. This way, 63 samples were received from Brazil, England, India, Norway, Sweden, USA and Russia. The data from studies of whole rock chemical composition, mineral composition and thermogravimetric analyzes showed that there was a wide range of chemical compositions within soapstone category and the detailed classification was needed.

The essential part of the experimental work was done in the VUKEII OY-project. The main goal in VUKEII OY-project was to investigate, how different soapstone types withstand thermal shock in terms of fireplace industry. For that, the Thermal Shock Resistant (TSR) test was developed since suitable test method did not exist. The extensive TSR-tests included total of 6396 test cycles. The fired soapstones were cooled down 5171 times by water, 939 times by air and 283 times by carbon dioxide ice. Approximately 2500 man-hours were required to execute the TSR-tests, since only three samples were possible to test simultaneously. The project included also comprehensive set of chemical, mineralogical and microstructural analyzes and determinations from 34 samples. In addition, physical attributes in relation to different soapstone types were studied: density, thermal conductivity and specific heat (by Professor Michael Gasik, Aalto University), thermal expansion and permanent length evolution. Acquired sample material represented extensively domestic soapstone types that are utilized economically at the moment. The material has been collected directly from outcrops, by receiving as donations and some by buying from the companies representing the industry of the project; PolarStone Oy, Nunnanlahden Uuni Oy and Vuoleri Oy which are situated in Savonranta, Juuka and Polvijärvi, respectively. In addition, a large share of samples has been drilled from outcrops in the Sotkamo, Puolanka, Kuhmo, Hyrynsalmi and Savonranta areas by Tuomas Havela and Antti Kärki. TSR-test cycles, mineralogical and microstructural analyzes and physical determinations were carried out by senior researchers Tuomas Havela and Anne Huhta and by research assistants Jani Kainulainen, Sanna Tikkakoski and Jukka-Pekka Ranta. In addition, thermogravimetric and differential thermal analyzes were performed by special laboratory technician Tommi Kokkonen in Process Metallurgy laboratory of University of Oulu. Impetus for this PhD-thesis came from the results of VUKE-projects and from the need of Finnish soapstone industry.

This thesis is a final contribution to “Sustainable Use of Soapstones”- research projects (VUKEI and II OY) in which the author has worked as a research assistant (VUKE I) and as a senior researcher (VUKEII OY) during 2006-2012. The projects were carried out in University of Oulu in collaboration with Geological Survey of Finland (GSF). They were funded by Tekes, Polarstone, Tulikivi Oyj, Vuoleri Oy, Geological Survey of Finland and University of Oulu, and completed according to their research plans. This thesis was carried out as a separate project with financial sponsors referenced in “Acknowledgements”-chapter.

1.2 Soapstones−Unexplored diversity

Soapstones have generally been described as carvable rocks with good thermal properties. Therefore, they have been used for example in vessels and carvings since the dawn of civilization, and later, also as a construction material in buildings, fireplaces and ovens (Storemyr & Heldal, 2002). Public has often considered these rocks mistakenly as only one kind of soft grayish rock although, geologically, soapstones are mainly low- to medium-grade ultramafic metamorphic rocks comprised primarily of talc, but may contain considerable amounts of other minerals, such as carbonate, serpentine, amphibole and chlorite, depending on protolith composition. The current definitions enable wide range of rocks with different mineral compositions to be classified as soapstones. So far, the detailed geological classification and nomenclature schemes for soapstones have been missing. Proper classification scheme for soapstones based on mineralogy would be valuable tool for the soapstone industry, as they could determine precisely which soapstone type they are utilizing. This is important because not all compositions and structures of rocks are suitable for the high-temperature environments, or to be used as a construction material under any circumstances. In the past decades, few efforts have been made to define soapstones (e.g. Storemyr, 1997; Kuzvart, 1984), but these have been mostly inadequate. Kärki et al. (2008) developed a tentative detailed classification scheme.

A wide range of chemical compositions and structures of soapstones can be found even within the same deposit. These attributes affect significantly on the thermal shock resistance of natural stones (Kärki et al., 2013). Lindqvist et al. (2007) described intrinsic properties, such as mineralogy, grain size, grain boundary shape, mineral orientation and porosity effecting on the durability of the rocks. Yavuz et al. (2010) and Soltan et al. (2011) have studied thermal effects on carbonate rocks, but the attention focused in limestones and marbles, which behave radically differently in high temperatures compared to magnesite soapstone, due to their structure and composition. Chaki et al. (2008) exposed granitic rocks to thermal wear and studied porosity, permeability and ultrasonic wave evolution in the heat-treated samples. However, the temperature they used was only 600 °C and the mineral phases differ too much for solid comparison to magnesite soapstone. Heating natural stones has also been used as a research method in terms of studying artificial weathering (Franzoni et al., 2013). However, these studies focused on different sandstones and limestones in rather low temperatures. Influence of high temperatures on natural stonework has been examined also from the aspect of building fires, in which thermal shock may occur to affect stone disintegration (Chakrabarti et al., 1996; McCabe et al., 2010; Ozguven & Ozcelic, 2013).

The material used in the inner parts of fireplaces and ovens must withstand temperatures over 1200 °C for many years and even for decades. Therefore, it was essential to develop a new thermal shock resistance (TSR) test for natural stones in which the temperature range is adequate to cover the working conditions in practice. With this test, TSR of different soapstone types was determined.

In addition to thermal wear of different soapstone types, the mineralogical changes of soapstone used in fire chamber and funnel walls are essential for durability and performance of fireplaces. It has been broadly known amongst the soapstone industry that the surface of magnesite soapstone hardens during the years of exposure to fire chamber conditions. Hence, periclase formation as one of the mineral alteration processes in the magnesite bearing soapstone fire chambers has been acknowledged already over hundred years ago, but closely studied only in the 1990´s (Gehör et al., 1994). However, the hardening with aging is not solely due to the periclase formation but is due to far more complex processes including other mineral alterations and reactions (Huhta et al., in press).

Most of the scientific papers dealing with the reactions in or between the components MgO, SiO_2, FeO and H_2O, generated by exposure to high temperature is by far ceramic or refractory related. Magnesium oxide has been studied over the decades and the focus is often directed to pure MgO-component (Vasilos et al., 1964; & Stokes, 1966) or pure enstatite (Lee & Heuer, 1987). More recently, concentrating in this field, elevated temperatures have been used to study steatite-based ceramics (Reynard et al., 2008; Mielcarek et al., 2004; Gökçe et al., 2011). In addition, the reactivity of light burnt magnesium oxide has been assessed by Chau & Li (2008).

In their study of "Sintering behavior of periclase-doloma refractory mixes", Tomba Martinez et al. (2009) showed that refractory materials containing periclase and doloma had higher mechanical strength and lower porosities at room temperature in the sample, which had the highest iron oxide percentage. Hydration resistance has also been studied using high temperatures. Kashaninia et al. (2011) and Aygül Yeprem (2007) concluded that added iron oxide improved the hydration resistance of magnesia-doloma refractories. Bessonov & Bessonova (1981) carried out the study of change in the MgO/FeO-ratio, during heating of periclase and wüstite. They showed that the percentage of magnesioferrite increases up to 1025 °C. Further increase of temperature started to dissolute magnesioferrite rapidly back to periclase. Magnesioferrite has been studied widely in the past, related to sintering of magnesium oxide (Wirtz & Fine, 1968; Woods & Fine, 1969; Kruse & Fine, 1972; Chaudhuri et al., 1999). Regarding this study, Table 1 shows formulas and relevant physical attributes of the most important primary minerals and heating products.

Table1. Formulas and physical attributes of the most important primary minerals and heating products of studied samples.

Primary mineral	**Formula**	**Density (g/cm3)**	**Hardness (Mohs scale)**
Magnesite	$MgCO_3$	3	4
Talc	$Mg_3Si_4O_{10}(OH)_2$	2.75	1
Chlorite	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	2.65	2-2.5
Magnetite	$Fe^{2+}Fe^{3+}{}_2O_4$	5.15	5.5-6
Product			
Periclase	MgO	3.78	6
Wüstite	FeO	5.7	5-5.5
Magnesioferrite	$MgFe^{3+}{}_2O_4$	4.65	6-6.5

In the field of ceramics and refractories, considerably amount of research has been published on thermal effects on synthetic or pure natural minerals solely, but very little information is available about thermal impacts on natural stones with their inner impurities, complex compositions and structures. In their study of physico-mechanical properties of high-temperature treated rocks, Liu & Xu (2015) adduced the need of practical engineering for increase the knowledge of high-temperature effects on physical behavior of rocks. The changes in mechanical properties of rocks exposed to high temperatures have raised attention since they are often unwanted in areas of geological engineering (Alishaev et al., 2012; Bellobede, 2006; Funatsu et al., 2004). In contrast, in the consensus of the theme of this thesis, the changes occurring in magnesite soapstones after high-temperature exposures and cooling cycles are, in fact, beneficial and needed.

1.3 Objectives of the study

The main objective was to study the mineralogical and structural diversity of soapstones (Fig. 1). In addition, this thesis addresses the research problem regarding the changes occurring in magnesite soapstone, especially on their surfaces, when used as construction material in fire chambers. The thermal wear of different soapstone types is also considered in this study. Following research questions are addressed in the separate research articles:

1. To develop a detailed classification scheme for soapstones based on the absolute volumes and relative quantities of main minerals. (**Paper I**)
2. To introduce a new method for determining thermal shock resistance of naturals stones, especially of soapstones, and to study how the different microstructures and chemical compositions of magnesite soapstone effect on the rock capacity to resist thermal shock. (**Paper II**)
3. To examine what mineral alterations and reactions lead the surface of magnesite soapstone to strengthen and harden in use as a fire chamber wall material over the years. (**Paper III**)

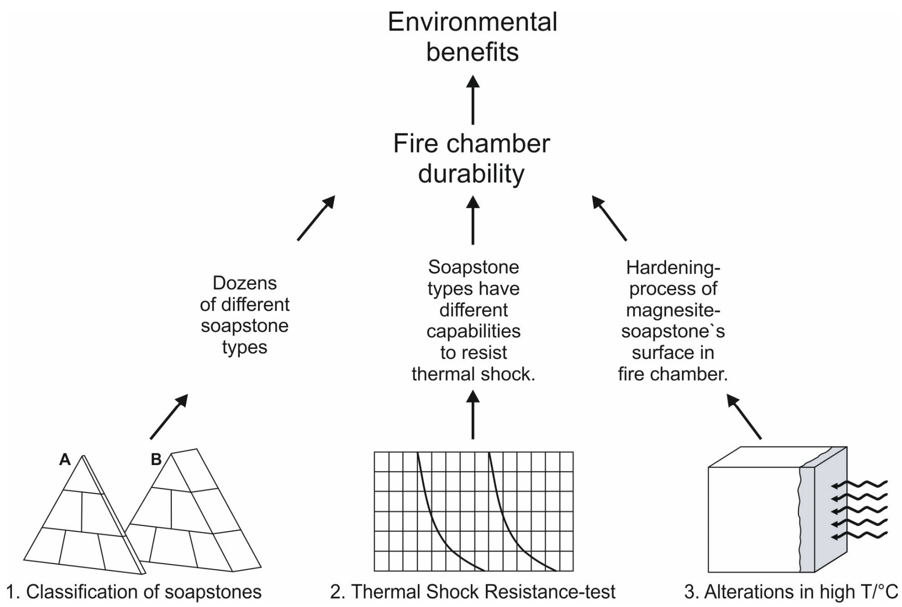

Figure 1. In addition to classification and nomenclature scheme providing a new tool for geological use, the aims of this thesis are to raise awareness about the compositional and structural diversity amongst soapstones and to highlight that utilizing natural magnesite soapstone in high-temperature applications is environmentally friendly (withstands well extremely high temperatures that leads to more particulate-free combustion, high capacity to reserve heat decreasing the need of firewood quantity).

1.4 Sampling and geological setting of the Nunnanlahti study area

For the thermal shock resistance test and for the classification of soapstones, samples were collected as described in the Introduction-section during the VUKE-projects. For the study of mineralogical alterations, the samples were taken from the selected fireplace construction, which has been in use during the years 1945-2009. The material used in this fireplace is originated from Nunnanlahden Uuni mine.

The Nunnanlahti where the study area is located is a small village in Northern-Karelia, in eastern Finland (Fig. 2). The ultramafic rocks in the area were first studied by Haapala (1936) and Wiik (1953). More recent attention of the Nunnanlahti area has focused on geochemistry, mineralogy and metamorphism (Wennerstrand, 2000; Lipponen, 2000). The soapstone massif occurs in the Nunnanlahti suite, which is a small Archean greenstone belt composing predominantly basaltic metavolcanic rocks (Pekkarinen et al., 2006). The belt is in contact with Archean granitoids and Paleoproterozoic metasedimentary rocks. Furthermore, Paleoproterozoic mafic dikes are cutting the Nunnanlahti Suite rocks. Ultramafic rocks, such as soapstone and serpentinite form approximately 250-m-wide (rarely 700 m) lens-shaped bodies and were originally dunites. Dunitic rocks were thoroughly serpentinized and afterwards partially altered to talc-carbonate rocks. The Nunnanlahden Uuni soapstone mine is located close to the margin of the greenstone belt, on the hanging wall side of the Nunnanlahti Shear Zone.

Geologically, Nunnanlahden Uuni mine (63°10’20.6” N 29°26’35.4” E) is situated in the NW-SE-trending, 1.4 km long and 0.7 km wide soapstone massif. Mafic and felsic volcanic rocks occur in the west side of the massif, whereas mafic volcanic rock and serpentinite occur in the eastern side. In the previous studies Kojonen (1986) and Wennerstrand (2000) reported metasomatic biotite-chlorite black-wall reaction zone at the tectonic contact between soapstone and mafic volcanic rock. Width of this reaction zone can vary from 0.3 to 0.5 meters.

Numerous different soapstone types are recognized in soapstone massifs in the Nunnanlahti area. The same variation occurs also in the Nunnanlahden Uuni mine site. Magnesite dominating soapstones differ from others both by mineral composition and microstructure. Also, brecciated serpentinite and chlorite schists occur as few-meter-wide fragments or zones within the soapstone deposit. In addition, tremolite-bearing schist exists locally between the contact of soapstone and serpentinite. Accessory minerals such as chlorite, chromite and magnetite are common. Wennerstrand (2000) reported chlorite-rich, folded and boudinaged bands, which are intensively altered mafic to ultramafic dikes cutting the soapstone. Also 10-

cm-thick chromitite lenses occur in the soapstone massif. As the chlorite bands, the chromitite bands are also boudinaged, brecciated and folded (Wennerstrand, 2000). Wennerstrand (2000) interpreted those to be originally small podiform chromitite bodies or layers of stratiform chromitite.

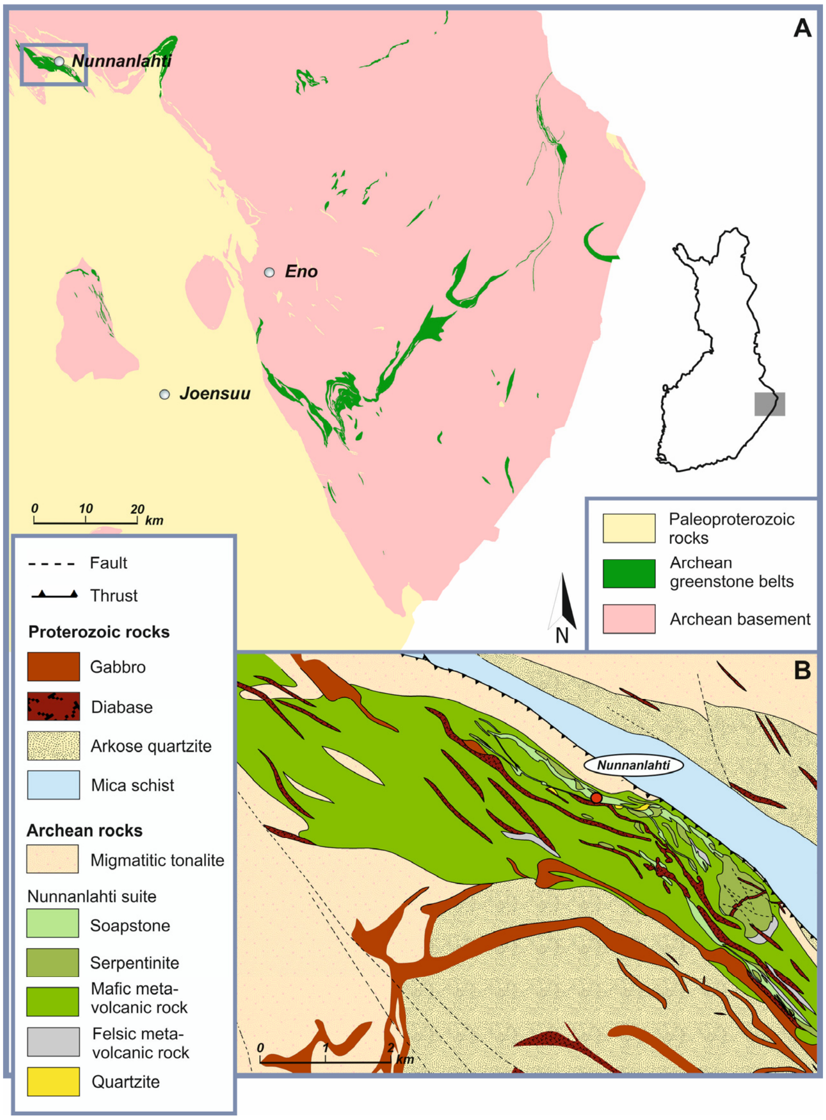

Figure 2. Regional distribution of greenstone belts in Northern Karelia, Finland (A). A soapstone massif with Nunnanlahden Uuni mine (red dot) and geological environment of the Eastern soapstone massives (B). Modified after DigiKP version 2.1.

2. SCIENTIFIC BACKGROUND

This chapter presents a literature review on physical properties effecting thermal behavior of soapstone types.

2.1 Microstructures in soapstones

Microstructures effect significantly on the most geotechnical properties of a rock. Soapstones and their microstructures are formed during metamorphism and deformation. Based on the way of their formation, the microstructures in soapstones are called secondary structural elements. These elements can be divided into granoblastic (unoriented) microstructures, planar foliations and lineations (Passchier & Trouw, 2005).

Mineral grains with equal dimensions have formed by re-crystallization in *Granoblastic microstructure*. Interfaces between grains can be sutured and interlocked to each other. Granoblastic texture can form by diagenetic alteration or by solid re-crystallization, if no deviatoric stress is affecting on the rock. Based on the predominant form of the mineral grains, granoblastic texture can be further divided into more detailed subclasses.

Secondary planar microstructures are called *foliations*. These are formed due to systematic orientation of planar or slab-like minerals in certain plane. Different foliations develop relatively easily to sheet silicates in soapstones, such as talc, chlorite and serpentine. They are divided based on the average grain size of the rock and the intensity of differentiation of dark and light mineral species to their own bands or layers (Passchier & Trouw, 2005). Based on Fossens, (2010) classification, there are three main foliation types: Cleavage with the particle size below< 0.1 mm, schistosity 0.1−2 mm, and banding, in which the dark and light mineral bands or layers are macroscopic (Fig. 3). Orientation can form thoroughly into the whole rock mass during deformation. This is called continuous or pervasive foliation. The other extremity is represented by spaced foliation in which the foliated bands, called cleavage domains, occur as extremely narrow seams in otherwise completely undeformed rock (Fig. 4). These undeformed relict bands are called as microlithons. To describe these attributes, applicable variables are an average frequency (spacing), shape and volume percentage of cleavage domains, spatial relations between cleavage domains and transition between cleavage domains and microlithons (Powell, 1979; Borradaile et al., 1982).

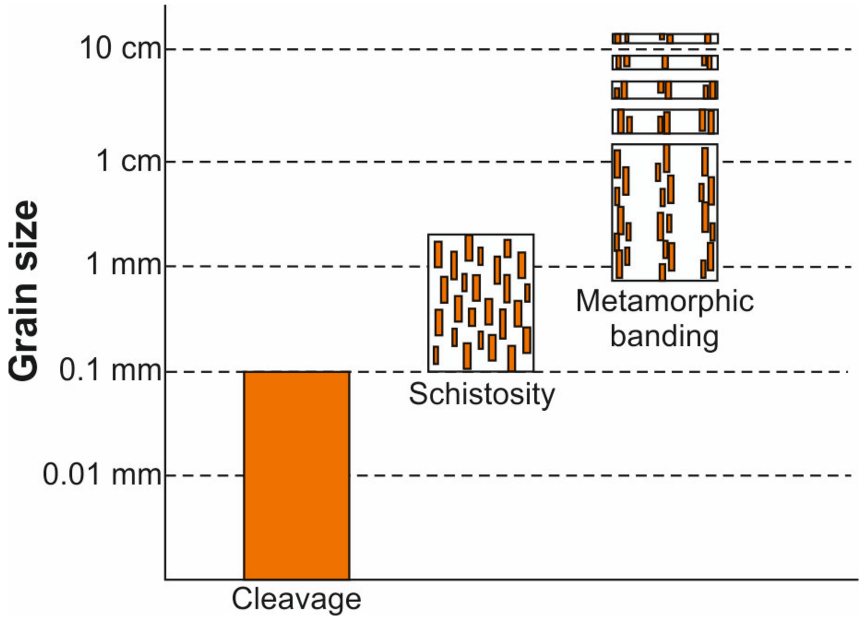

Figure 3. Grain size related foliation types after Fossen (2010).

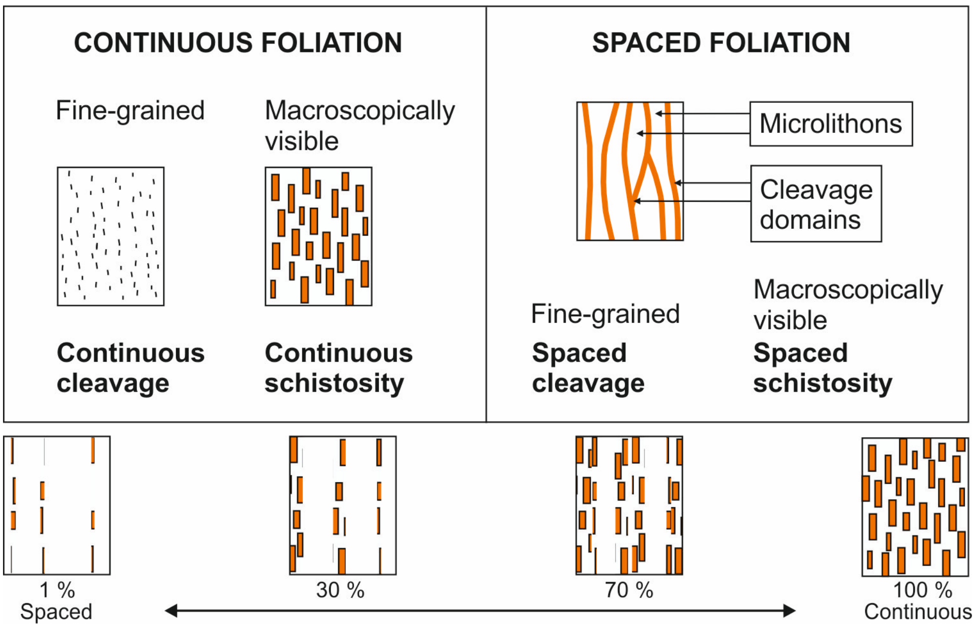

Figure 4. Schematic division of secondary foliations after Powel (1979) and Borradaile et al. (1982).

Lineations are linear features, which occur thoroughly in a rock body. According to Piazolo & Passchier (2002), they can be divided into two major groups: Object and trace lineations (Fig. 5). Object lineations can form by anisotropic minerals (grain lineation) or they can be formed by different crystal deformation mechanisms (Passchier & Trouw, 2005). These stretching lineations are further called as aggregate lineation and grain lineation with stretched isotropic minerals. Trace lineations form either by small scale folding of planar structural element (Crenulation lineation), or by two thorough planes intersecting one another (Intersection lineation) (Piazolo & Passchier, 2002).

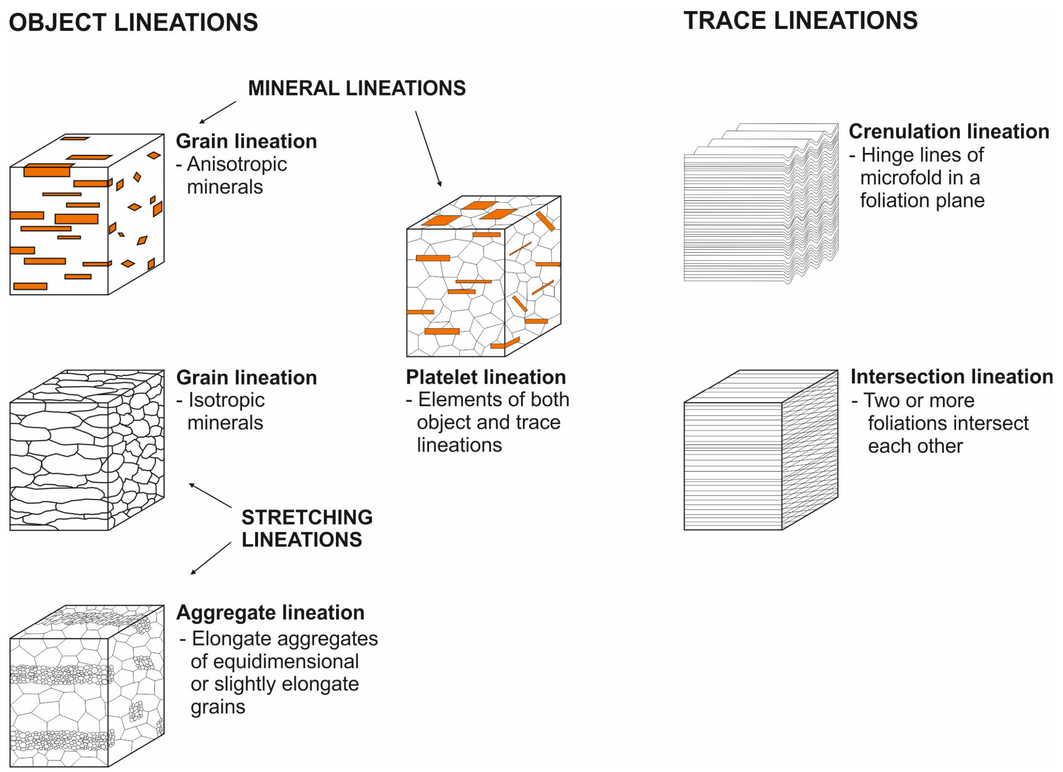

Figure 5. Schematic division of lineations after Piazolo & Passchier (2002).

2.2 Thermal shock resistance

Thermal stress is the stress that takes place in a specimen when it is subjected to temperature changes. Hence, thermal shock resistance is the maximum leap in the surface temperature (°C) that the solid material can withstand without breaking. The existing literature on thermal shock resistance of solids is quite extensive, but focuses on ceramics (Lu & Fleck, 1998; Tang et al., 2016; Zhu et al., 2017) and on metals (Cverna, 2002). There are recent studies (e.g. Wang et al., 2016) concerning thermal shock of natural stones, although they are executed in relatively low temperature to simulate natural weathering conditions. However, the behavior of rock as a crystalline material subjected to thermal stress is essentially similar. In general, thermal shock resistance of solid material depends on duration of thermal exposure, specimen size, heat transfer coefficient, tensile strength, fracture toughness, elastic modulus, thermal diffusivity, thermal conductivity and thermal expansion coefficient (Lu & Fleck, 1998). With natural stones, thermal shock resistance depends also on intensity, form and direction of foliation or foliations, grain size, lattice preferred orientation, porosity and chemical composition (Lindqvist et al., 2007). When heated, material starts to warm up from its surface. Heat is gradually conducting towards the center according to above mentioned attributes. Therefore, thermal gradient between the interior and the surface of the material causes these parts to expand unevenly. Much greater temperature differences occur however, when material is cooled down by water quenching. With this method the thermal gradient is significantly more intense than in the heating process and produces greater tensions between cold and hot parts. Therefore, in thermal shock resistance tests with water quenching, samples break down mainly during the cooling process. The intensity of thermal gradient is inversely proportional to the cooling time of the material.

The need of proper thermal shock resistance test of natural stones has been noted by several researchers. Lindqvist et al. (2007) noticed the lack of a functional tool to select stones with suitable attributes for their intended purpose as a construction material. Moreover, Franzoni et al. (2013) concluded that in terms of testing natural stones, the heating conditions should be tailored to the specific rock type in order to obtain comparable data. To fill this void, the development of the thermal shock resistance test was initially started during the TEKES-funded VUKEII-project (Kärki et al., 2013). They determined the reaction temperatures of mineralogical phase alterations of different soapstone types with thermogravimetric and differential thermal analyzers. The essential reactions occurred mainly between 540°C and 1000°C. In terms of this thesis, these temperatures are important, because burning wood efficiently in a fireplace, wall material reaches these temperatures in a combustion chamber. Using wood as fuel, the surfaces of the hottest parts can be exposed to combustion gases with temperatures over 1200 °C (Kärki et al., 2013). As part of the fireplace construction, soapstone material must withstand that kind of stress as well as possible for a long period of time and for a great number of heating cycles.

2.3 Density

Physical properties of different rock forming minerals have been reported in multiple handbooks (e.g. Schön, 2015; Ahrens, 2013). After Liu & Xu (2015), density of a rock gradually decreases with temperature elevation, but dehydration and bonding amongst components can also affect increasingly on rock`s density. Schön (2015) showed that the acidic components in rocks generate lower densities than basic ones. This was demonstrated also by Kärki et al. (2013), who found that as ultramafic rocks, soapstones have relatively high densities compared to other rock types. In their comprehensive study physical properties of different soapstone types were investigated. They found that the average density of magnesite soapstones was 3 g/cm^3, whereas the lowest values were determined from amphibole and serpentine soapstones (2. 9 g/cm^3 and 2.8 g/cm^3 in average, respectively). The density of a mineral depends on the atomic weights and proportions of its elements and its crystal structure. Hence, the density of a rock depends on mineral composition, chemical composition of minerals and porosity.

2.4 Thermal conductivity

Heat can be transmitted by radiation, advection and conduction (Clauser & Huenges, 1995). Heating polycrystalline material above 600 °C, radiation of heat starts to take over from overall heat transfer (Clauser & Huenges, 1995). Within single crystals, it becomes effective already in 200–400 °C. Thermal conductivities (W/(m*K)) defined in laboratory circumstances at high temperatures generally contain this radiation component (Clauser, 1988).

It has been known for decades, that thermal conductivity varies inversely with temperature (Birch & Clark, 1940). Respectively, Kärki et al. (2013) showed in accordance with Gummow & Sigalas (1988) and Clauser & Huenges (1995) that thermal conductivity of an untreated natural rock decreased with increasing temperature. Their study also revealed that magnesite soapstones have the highest thermal conductivity values measured in room temperature and in 300 °C compared to other soapstone types. High thermal conductivity is due to relatively high oxide (magnetite and chromite) and magnesite percentages. According to Kärki et al. (2013), thermal conductivity was 6-21% lower, when measured perpendicular to the direction of the foliation in the rock. As well as density, thermal conductivity of a rock decreases faster with temperature when felsic mineral phase, like quartz is present. Naturally, thermal conductivity is controlled by the mineral composition of the rock, but also by pressure, degree of saturation, pore fluid and anisotropy (Clauser & Huenges, 1995).

In his inclusive study Horai (1971) found that, due to specific crystal structures and chemical formulas, thermal conductivity of minerals can be determined with a much greater accuracy than that of rocks. However, he also noticed that the lattice impurities and the sample size set challenges to measurements, because of the generally low amount of large crystals. When scrutinizing thermal conductivity of unfired talc, it behaves the same way as rocks in general; the results show a linear decrease with increasing temperature. However, in the range of 27 - 627 °C, thermal conductivity of fired talc increases with temperature elevation (Gummow & Sigalas, 1988). In more recent study by Yoneda et al. (2012), they found that thermal conductivity of talc was similar to olivine despite of a talc´s sheet silicate structure.

2.5 Thermal expansion

Thermal expansion (1/°C) is the tendency of matter to change its shape, area, and volume in response to a change in temperature. The coefficient of thermal expansion describes how the size of an object changes with a change in temperature. Thermal expansion coefficient measures the change in volume of the material as a function of temperature at a constant pressure.

Thermal expansion occurs when temperature changes alter the shape and increase volume of a system. Thermal expansion of minerals can be either isotropic, coefficient of thermal expansion being constant in every direction or anisotropic (crystal structures other than cubic) when the coefficients of thermal expansion are unique in the directions of different crystal axes. According to Markgraf & Reeder (1985), for the *a*-axis of magnesite, coefficient of thermal expansion is 6.75×10^{-6}/°C and for *c*-axis 22.9×10^{-6}/°C, respectively. Thus, the thermal expansion in magnesite crystal is three times greater in the direction of *c*-axis. Coefficients of thermal expansions of carbonate minerals have been reported in several handbooks (e.g. Skinner, 1966; Fei, 1995), but regarding talc, the other main mineral of soapstones, data from thermal expansion are rare. Pawley et al. (1995) discovered that thermal expansivity of talc is the most intensive parallel to *c*-axis. Talc is comprised of parallel sheets of SiO_4-tetrahedras. OH- groups and Mg-cations are located in between the SiO_4-sheets. They are compounded to SiO_4-sheets by weak Van der Waals forces. This is also the reason for perfect {001} cleavage and greasy feel of talc.

Again, the thermal expansion measurements of minerals are more accurate than the whole rock measurements, due to different expansions of adjacent grains in whole rock. Dane (1942) concluded that heating the rock causes internal fractures and increasing porosity. Consequently, the measured attribute is therefore porosity rather than the actual thermal expansion of the sample. However, the whole rock thermal expansion measurements create information about relative differences between rock types.

Thermal expansion behavior is anisotropic in all the main minerals of soapstones. It is controlled by the mineral phases and by the microstructure. Kärki et al. (2013) investigated the thermal expansion and the permanent length evolution of soapstones with different mineral compositions. The study was done by optical dilatometer in which the samples of different soapstone types were heated from room temperature to 1150 °C. Changes in the sample dimensions were captured as dimensionally accurate images which the automatic application photographed along increasing temperature at the rate of 1 image/ 1 °C. They showed, that thermal expansion of studied soapstone types did not rise above 2 %, when the samples were heated to 500 °C. Changes in the dimensions of carbonate and serpentine soapstones were also minor (2-3% at the most) up to 1100 °C. However, in this temperature chlorite rich soapstones expanded up to 7-8 % from their original dimensions. As for the permanent changes the results were relatively similar. Dimensions of serpentine soapstones were reduced 2 % in every direction at 1100 °C. This was also the situation amongst the carbonate soapstones, but only in the direction of the foliation. Chlorite soapstones heated to 1100 °C showed permanent of 8 % increase in dimension perpendicular to foliation, whereas there was a 4 % reduction in the direction parallel to foliation. Thermal expansion causes rock density to decrease and simultaneously porosity to increase, due to increasing amount of microfractures induced by heat. This also explains, why thermal conductivity decreases with temperature (Kranz, 1983).

2.6 Thermal decomposition

Thermogravimetric analysis (TG) is a technique in which the mass of a sample is measured as a function of increasing temperature. Changes in a mass occur when gaseous phase is released from the system due to mineral reactions taking place at different temperatures. Nature and number of volatile products released from a substance can be measured with a gas analyzer. By the differential thermal analysis (DT), it is also possible to determine the amount of energy that is produced or consumed during mineral reactions. The temperatures of mineral phase changes can be determined with these techniques (Földvári, 2011).

In this study, the importance of mass changes lies in the temperature of thermal decomposition of the main minerals of soapstones. Based on literature, dehydroxylation of talc occurs typically between 800 °C and 1000 °C (Wesolowski, 1984; Földvári, 2011; Liu et al., 2014). The reaction of dehydroxylation and structure decomposition is:

$$Mg_3Si_4O_{10}(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O$$

There has been some debate over the thermogravimetric results for instance the stages of talc dehydroxylation. Bošković et al. (1968) and Ward (1975), reported only one dehydroxylation stage, Ishii et al. (1974) found two stages and Avgustinik & Vigdergauz (1948) three stages of dehydroxylation. In more recent study by Zhang et al. (2006), infrared spectroscopy results of talc decomposition were consistent with the thermogravimetric measurements of Ward (1975). He showed that the loss of mass starts near 750 °C and ends at 1100 °C. In their nanoparticle and electrical conductivity related studies Dellisanti & Valdré (2010) and Wang & Karato (2013) found that TG-DG curves reveal a minor weight loss at 120 °C caused by dehydration of absorbed water, but the major weight loss due the dehydroxylation of talc occurred between 800- 1000°C. Consistent with those results, the data shows also a wide endothermic differential scanning calorimetry (DSC) peak at 890 °C. Liu et al. (2014) concluded that pure talc starts to alter to enstatite at 800 °C and at 1000 °C, it is completely dehydroxylated.

Thermal decomposition of another main mineral of soapstone, magnesite, has also been described widely in literature (e.g. Sheila, 1993; Turčániová et al., 1996; Liu et al., 2012; Tian et al., 2014). The most characteristic property of carbonates is the endothermic decomposition with the liberation of CO_2 (Webb & Krüger, 1970). Thermal decomposition of magnesite occurs at 620-650 °C according to the reaction:

$$MgCO_3 \rightarrow MgO + CO_2$$

In addition, Kulp et al. (1951) reported that iron in magnesite elevated the decomposition temperature whereas other foreign cations seemed to decrease it. In their thermal study of carbonate minerals Kulp et al. (1951) have noticed that particle size of pure crystalline magnesite has effect on thermal decomposition temperature. Microcrystalline magnesite decomposed at slightly over 700 °C, whereas visible grained specimens decarbonated already at 680-700 °C. In addition, Demir et al. (2003) studied the particle size related on magnesite decomposition, but they investigated the effect on reaction kinetics and reported that activation energy decreased with decreasing particle size. In more recent studies Liu et al. (2012) and Tian et al. (2014) showed that decomposition of magnesite starts at 400 °C and according to Tian et al. (2014) it is completely over at 700 °C. Liu et al. (2012) presented that decomposition continues up to 800 °C. In addition, Tian et al. (2014) reported that CO_2 –evolution was consistent with TG- curves that shifted to higher temperatures with increasing heating rates. Both studies agree that thermal decomposition is a one-stage reaction.

It is not always unambiguous to determine a reaction temperature by thermogravimetric methods from one phase when the sample composes also other water containing minerals. Furthermore, impurities of natural minerals can have effect on the results. In their extensive study of thermal properties of soapstones, Kärki et al. (2013) have investigated phase alterations in various soapstone types at different temperatures by TG- and DT- analyzers. They heated the samples from room temperature up to 1200 °C with heating rate of 20 °C min^{-1}. Also, volatiles released during decomposition, such as H_2O and CO_2 were analyzed by TGA. Kärki et al. (2013) showed that dehydroxylation of talc starts in different soapstones with different compositions between 800 – 850 °C. Moreover, there was one sample in which talc occurred in two populations with different iron content (under 1 % and 4.0-4.5 % of FeO). The dehydroxylation of the iron poor population started slightly over 800 °C. However, for the iron rich population decomposing started as late as at 1000 °C (Fig. 6)

In agreement with the results of Kulp et al. (1951), Kärki et al. (2013) reported that the decarbonation temperature of magnesite is directly proportional to its iron content. In their study, magnesite decomposition started from 540 to 600 °C, being higher in iron rich magnesites. Kärki et al. (2013) analyzed serpentine and chlorite soapstones as well and found that the iron percentage of those minerals also correlates positively with their dehydroxylation temperatures.

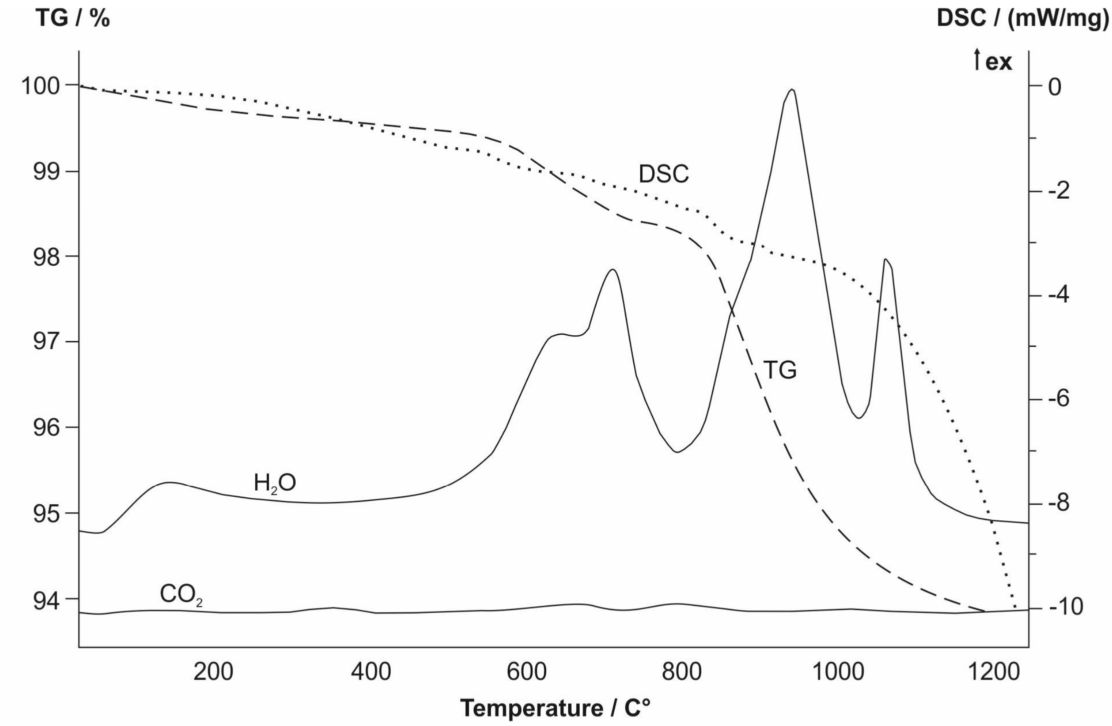

Figure 6. Results of thermogravimetric (TG), differential thermal (DSC) and gas phase (H_2O, CO_2) analyses from amphibole bearing oxide soapstone. ↑ex = exothermic reaction upwards.

3. EXPERIMENTAL METHODS

3.1 Thermal shock resistance test

With this study, the test method was developed further to fully functional form for determining the resistance of a rock to rapid temperature changes. The test is developed based on the existing standard DIN51068, but with possibility to tailor the testing temperature eligible for the specific rock type and structure. The major part of the soapstone samples from VUKEII-project were utilized during the work. In the study of Kärki et al. (2013), the samples represented as many different soapstone types, compositionally and structurally, as possible. The sample material within this thesis was limited to concern only magnesite soapstones with several microstructural variations. It was already known due to the TSR-test results and practical experience that at least the magnesite soapstones can at their best, withstand major temperature gradients. Confining the sample set with very narrow variation in chemical composition it was possible to focus to the effect of structural attributes on their thermal shock resistance. The developed procedure (Fig. 7) is as followed:

1. A cylindrical specimen of a natural stone with a diameter of 52 mm and a height of 50 ± 2 mm is dried at 110 ± 5 °C in a hot cabinet (Memmert, maximum heating capacity 220 °C) for at least eight hours.
2. After drying, the specimen is heated in an electric furnace (Nabertherm N 50, maximum heating capacity 1200 °C with Program Controller C7) for 15 minutes. The temperature is set at 600–1100 °C depending on the type and structure of the soapstone sample. Temperature shall not fall more than 20 % from the selected level due to opening the furnace door.
3. Cooling is implemented by plunging the specimen directly from the furnace into running water at 5–10 °C for 3 minutes.
4. In the next stage, the specimen is placed back to the hot cabinet to be dried for 30 minutes.
5. The heating-cooling-drying cycle described above is repeated for each specimen until it broke down into two or more pieces. The test is discontinued, if the specimen remains intact after 30 test runs. In that case, the test is continued by raising the heating temperature by 100 °C.

As described above, the equipment for testing thermal shock resistance is very simple. In addition to a hot cabinet and an efficient furnace, operating the test requires a large container for water quenching. Temperature of the water medium is kept at 5–10 °C by constant circulation during the rock quenching. The result of the test is the TSW number, which is the number of drying-heating-cooling- cycles which the material withstands without breaking down. For tests made at different temperatures, the results were converted to values using the chart constructed by Kärki et al. (2013). A separate curve in this chart was composed by exposing one material type to different temperatures and finally the chart was finished with determinations made from several different material types. By using this chart, the result of a single test (TSW-number) can be converted to a TSR-number, which describes material´s capability to resist thermal shock. This way the results received in different temperatures are comparable to each other.

Because of the natural origin of the tested material, source of errors is related to possible heterogeneous structure of the rock. Large singular crystals inside the rock induce an early break down of the specimen, as well as pervasive and smooth foliation planes formed by e.g. deformed chlorite. In these cases, the TSR numbers indicate only the TSR of the heterogeneous matter, not TSR of the entire rock sample. Therefore, the smallest anomalies in the structure of tested rocks affect to some extent to their TSW numbers. Hence, only those sample sets were accepted as successful in which the standard deviation for the TSW number in the sample set representing one test temperature was 3 at the most. Repeatability of the test method has been proven by the 6396 test cycles. TSR number representing a sample set is determined by counting the average TSW number of at least five specimens representing the same homogeneous material type.

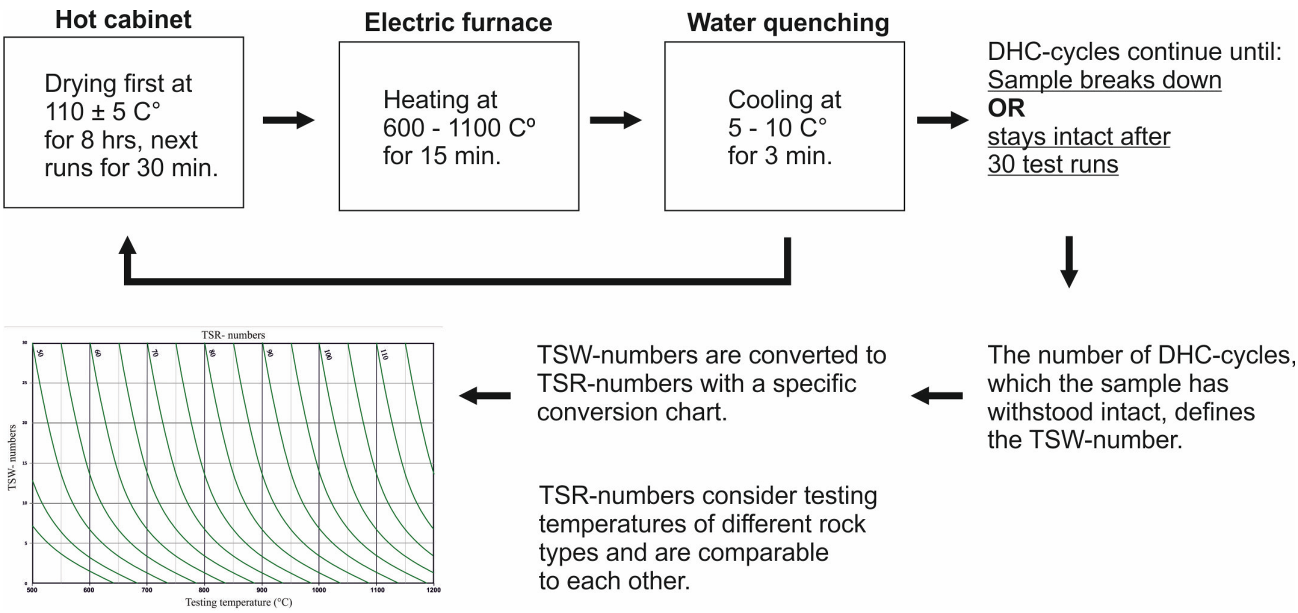

Figure 7. Thermal shock resistant test procedure and the determination of the TSR-number.

3.2 Mineralogical and microstructural studies

Among other applications, the electron probe microanalysis (EPMA) and the field emission scanning electron microscopy (FESEM) are universal methods in descriptive petrology and in mineral identification. Although functions of these techniques overlap significantly, priority of EPMA is to perform chemical analyses from selected areas of solid samples, but the FESEM is intended primarily for high resolution imaging (Reed, 2005). Advantages of these techniques are considerable. Unlike several other analyzing methods, these are non-destructive techniques. Usually the same sections can be used in EPMA and FESEM as in polarization microscope with none or minor modifications. Both EPMA analyses and FESEM images were performed at the Center of Microscopy and Nanotechnology in University of Oulu. Microanalyses were carried out on a Jeol JXA-8200 Superprobe with an acceleration voltage of 15 kV and a beam current of 15 nA. The peak counting time was set at 10 and 5 s at the background. Probe size was set at 5 μm. Microstructural features and compositional variations were investigated on a Zeiss Ultra

Plus field emission scanning electron microscope with backscattered-electron imaging. Topographic nature of the samples was also studied with secondary-electron imaging. With FESEM the acceleration voltage was 15 kV and the beam current 15 nA.

X-ray powder diffraction (XRD) is widely used in mineralogical, ceramic and in refractory relations (Ferrage et al., 2006; Gleason et al., 2008; Shatskiy et al., 2015; Chen et al., 2016). In this study XRD is primarily used for phase identification of minerals with and without alteration and for determination of crystal dimensions. It was also possible to determine the percentages of the different mineral phases, because analyzed samples were whole-rock powders. In addition, the grain sizes of fresh and altered carbonate soapstone were compared.

4. REVIEW OF THE ORIGINAL PUBLICATIONS

The paper I proposes a new definition, classification, and nomenclature schemes for soapstones. Throughout the times, soft and talc-containing rocks have considered as soapstones, although their mineral composition and structure varies tremendously. Due to this variation, also the range of their physical properties is wide. Hence, classification of soapstone should be based on mineral composition as also in many other rock types (e.g. igneous rock using Streckeisen (1976) classification). In addition, with the aid the classification provides, soapstone industry can optimize the use of different soapstone types for appropriate applications.

Following the International Union of Geological Sciences, Subcommission on the Systematic of Metamorphic Rocks (IUGS-SCMR) recommendations and naming policies, it is proposed that soapstone must include 35 – 75 vol.% talc. If hard silicates like e.g. serpentine or amphibole are present, their contents together cannot exceed 35%. Further division is done by ternary diagram with magnesium and iron containing oxides, chlorite and carbonate as the end members. If a soapstone contains over 5% hard silicate, the name of the silicate is placed in front of the name of the soapstone (Fig. 8). The classification is based on a large amount of compositional data from Finland, Norway, Sweden, England, Brazil, India, USA and Russia.

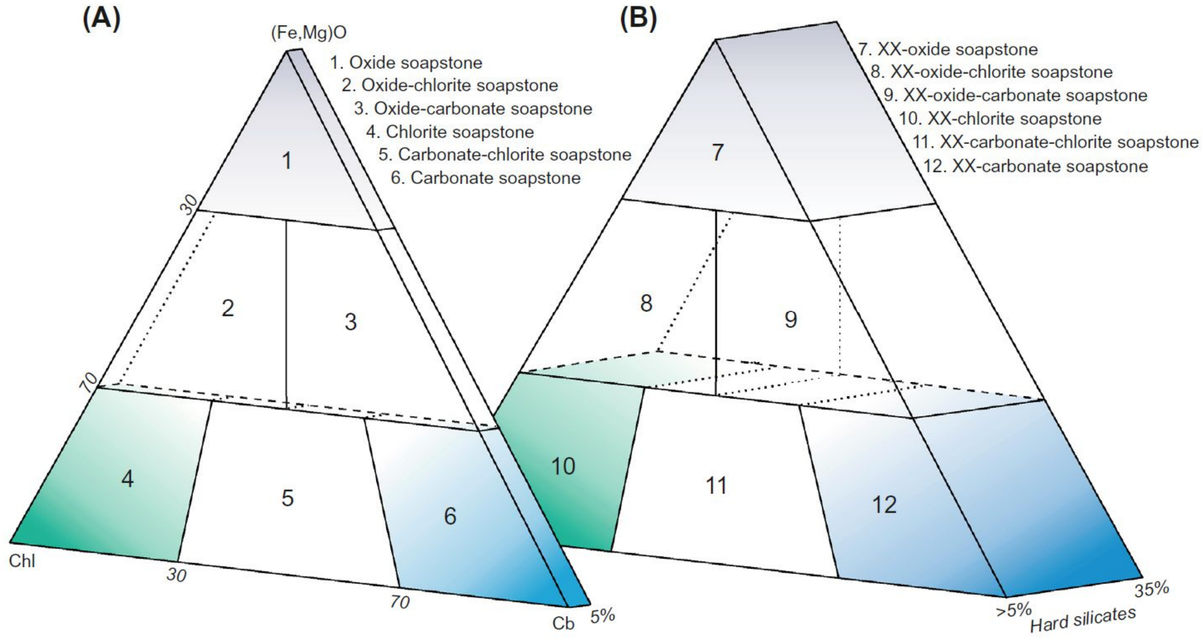

Figure 8. The soapstone classification diagram based on relative compositions of oxide, chlorite and carbonate (modified after Kärki et al., 2008). Soapstone containing hard silicate minerals. A) 0–5 % and B) > 5–35 %. XX is the name of major additional silicate species.

The paper II introduces a new method that was developed to measure thermal shock resistance (TSR) of any natural stone, but in particular the soapstone types which are being used as a construction material of fireplaces. In the paper II, 26 magnesite soapstones were tested in final test runs in order to evidence the functionality of the method, and to investigate, what are the microstructural thermal shock controlling parameters.

The thermal shock resistance test is based on creating steep temperature gradients by heating the material and cooling it down very quickly. Appropriate temperature is selected for materials with different mineralogical and structural characteristics and the results are converted to values that are comparable to one another regardless of testing temperatures. The new TSR-test was designed based on the method described in standard DIN 51068 (DIN 51068, Testing of ceramic materials, 1976) with a difference that it allows the employment of multiple temperatures. Fig. 9 shows magnesite soapstone after 18 TSR test cycles. In addition to periclase formation and the reaction between magnesite and talc, no other major sings of alteration can be seen.

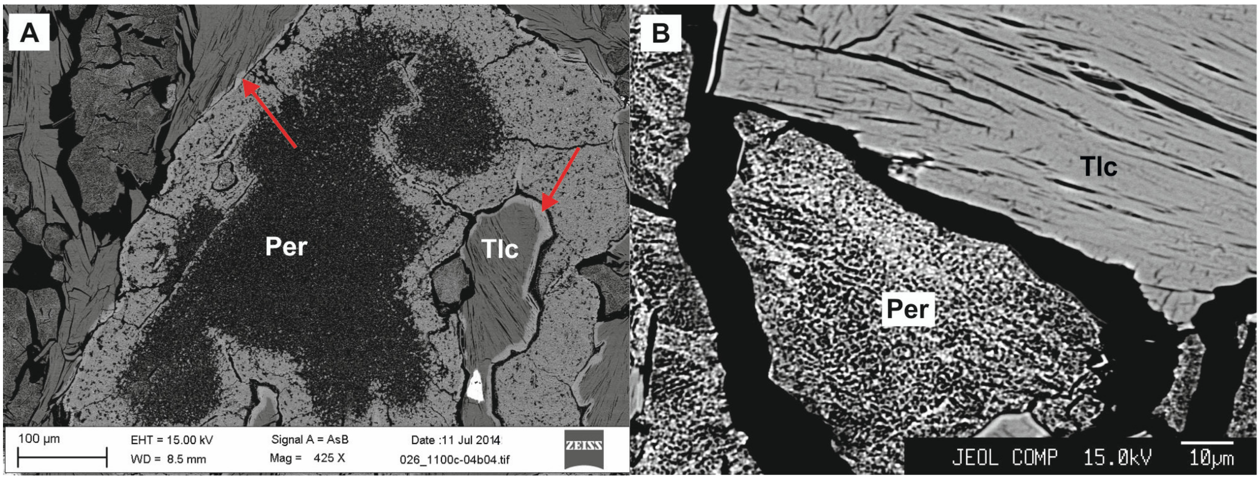

Figure 9. Magnesite soapstone after 18 TSR test cycles. A) Red arrows indicate the reaction between magnesite and talc (FESEM image). B) Microcracks surrounding periclase grains are empty (BSE image). Per = periclase, Tlc = talc

This article concentrates also on the attributes that are affecting on thermal shock resistance of carbonate soapstone. The contribution of chemical compositions and microstructures on the thermal solidity of the rocks was studied by microprobe and FESEM with chemical and structural aspects. It is evident that the microstructure of otherwise similar magnesite soapstones plays the most important role in thermal shock resistance. More specifically, attention should be paid on the attributes of secondary foliation. The short cleavage domains and the rough form of them support high thermal shock resistance of the rock, whereas long and planar form of cleavage domains contributes lower resistance, respectively. The chemical composition has only minor effect amongst the very coherent set of magnesite soapstone samples. The TSR increases with the incorporation of iron and magnesium into talc and magnesite phases.

The paper III represents the mineralogical alterations that have occurred on the surface of magnesite soapstone that has been subjected to fire chamber conditions for decades as a construction material of fire chamber wall. Repeated heating, slow cooling and humidity in the fireplace have over the years changed the chemical composition of the fire chamber wall rock´s surface. The cooperative actions of these changes have been detected to be beneficial since they harden the material.

Major element whole-rock data and detailed mineral analysis data are provided from the altered and fresh part of magnesite soapstone. The data of mineral analysis are presented zonally at different distances from the surface of the sample, hence they describe the gradually proceeding alteration. Based on the whole-rock data from the soapstone surface, iron-rich magnesite has been altered to ferropericlase. In addition, the microprobe data confirm that magnesioferrite and notable quantity of brucite has been formed. Furthermore, they indicate that there has been an intensive iron mobilization towards the surface of the sample and towards the rims of talc and ferropericlase aggregates. The data points to structure densification by FeO, ZnO and K_2O entering chlorite and talc-rims. In addition, brucite formation into microcracks of periclase and changing to serpentine near the surface increases the densification effect (Fig. 10). Compositions of burned biofuels have been influenced the hardening process as well. ZnO and K_2O have been released from biofuels along combustion gases and crystallized with pseudomorph aggregates on the surface of fire chamber walls. Figure 11 shows an equilibrium ferromagnesite- talc pseudobinary phase diagram (Holland & Powell, 1998) in which the microanalyses were used as endmembers of the bseudobinary. The diagram describes the theoretical reactions of these two mineral phases assuming that reactions happen in equilibrium. In practice, mineral phases separate due to volume change, and cannot react further together. That, and relatively short heating time of fire place would explain, why all the reactions in the Fig. 11 do not occur in actual magnesite soapstone.

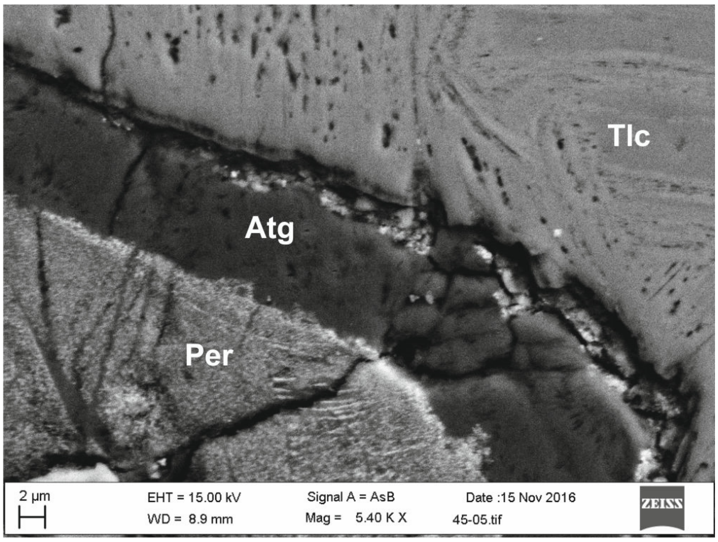

Figure 10. Microcracks surrounding periclase grains in magnesite soapstone used as a fire chamber wall rock for 60 years, have first filled with brucite, and later on serpentinized (FESEM image). Atg = antigorite, Per = periclase, Tlc = talc

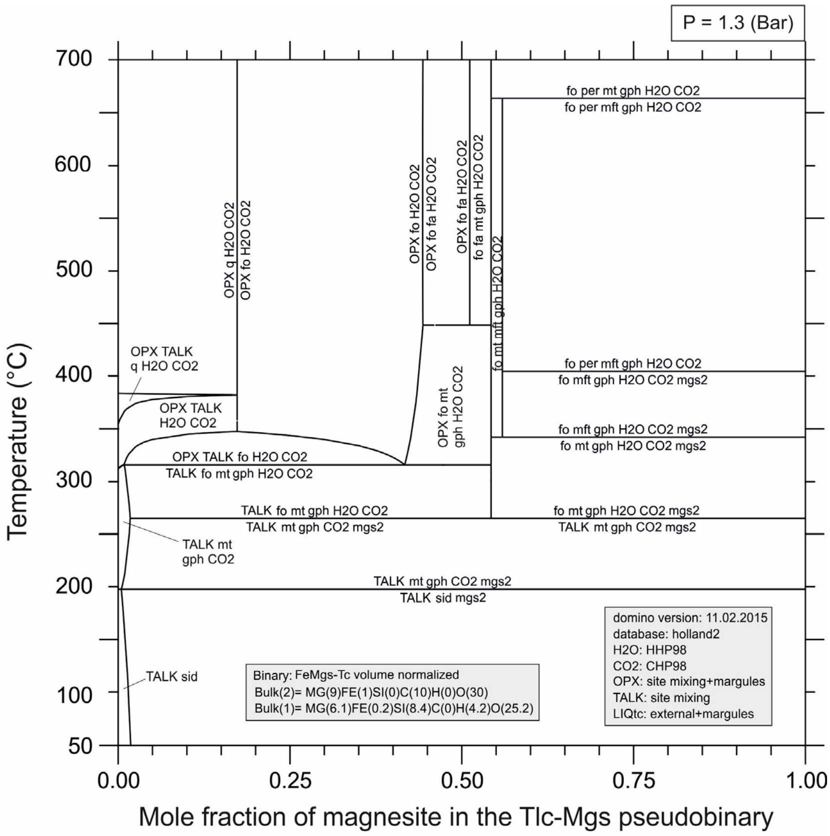

Figure 11. Equilibrium Ferromagnesite-talc pseudobinary phase diagram (Holland & Powell, 1998). Microprobe analyses were used as endmembers of the pseudobinary (Bulk 1 = talc, Bulk 2 = magnesite). gph = graphite, fa = fayalite, fo = forsterite, mgs = magnesite, mft = magnesioferrite, mt = magnetite, opx = orthopyroxene, per = periclase, sid = siderite.

5. DISCUSSION

Along with this study new innovations were developed; nomenclature and classification schemes of soapstones and a method for testing thermal shock resistance of natural stones. With the help of these implements, the soapstone samples were classified according to their mineral composition. Also, the TSR was determined, and the effects of microstructural and mineralogical variables to TSR were examined in the appropriate temperature that corresponds to conditions in which they are used in practice. In addition, the results confirm that the hardening of the surface of the magnesite soapstone fire chamber wall is mainly a complex combination of FeO-rich magnesite alteration to pseudomorphic aggregates consisting ferropericlase, magnesioferrite crystallization, brucite formation and alteration to serpentine, and iron enrichment with zinc and potassium additions into the rock surface via wood combustion gases.

The term "soapstone" has been used for rocks composed mostly of talc or talc-like mineral species (Wiik, 1953) and it is also applied to numerous talc-bearing, low- to medium-grade metamorphic rocks formed from the alteration of ultramafic igneous rocks (Vesasalo, 1965). There are also other previous definitions for these rocks e.g. (Kuzvart, 1984), but after Kärki et al. (2008) no strict and comprehensive one has been published earlier. Soapstones consist of a diverse set of mineral compositions and textures resulting wide range of different physical properties. This natural variation may cause the selection of unsuitable materials for high-temperature applications. In addition to geological void of having solid definitions, the soapstone industry has drawn attention to the present inadequacy and ambiguity of soapstone classification and nomenclature. This study was started by classifying the soapstone samples with the developed classification scheme in **Paper I** and then selecting the fine-grained, 40–60% talc and 35–50% magnesite containing soapstones for TSR-tests, since that is the rock type mostly used in the walls of fire chambers and funnels. Due to homogeneous mineralogy amongst the selected magnesite soapstones, it was expected that the reasons for lower TSR were mainly textural. Results show in **Paper II** that in agreement with Åkesson et al. (2003), the longer and the smoother the cleavage domains are, the faster the magnesite soapstones break in the test. However, evidently the presence of certain type of foliation was essential for staying intact in extreme conditions; high-TSR rocks include short cleavage domains with rough form of planarity. This is an essential finding hence, the importance of mainly microscopically visible foliation in the rocks that are expected high-refractoriness, is now acknowledged also scientifically. Thus, the fine grain size and granoblastic texture do not solely ensure high thermal shock resistance of these rocks. **Paper II** shows also that moderate crenulation cleavage and slightly elevated iron-contents in talc and magnesite phases affect favorably on the TSR of magnesite soapstones. Regarding the effect of iron, Kärki et al. (2013) gained similar results in their TG-analyses made from different types of soapstone. The durability supporting role of iron is demonstrated in accordance with Szczerba et al. (2015) and Behera & Sarkar (2015) also in **Paper III**. There, the hardness of the fire chamber wall rock´s surface has increased over time. The magnesite soapstone sample is studied zonally starting from the depth of 15 cm continuing up to the surface. Visible alteration is 30 mm thick from the surface. As the Figure 12A shows, the results indicate that iron crystallizes as magnesioferrite along the rims of iron-rich magnesite, turned to ferropericlase pseudomorph aggregates, occurring in the surface of a fire chamber rock. These findings are consistent with preliminary studies of Wirtz & Fine (1968), Kruse & Fine (1972) and Bessonov & Bessonova (1981). Iron tends to increase also in the talc-rims (Fig. 12B) and in chlorite from 30 mm depth towards the surface of the wall rock, where fire and combustion gases have had a direct impact to the wall rock. However, the hardening process is not solely due to iron mobilization. Since the construction material used in fire chamber is natural stone with multiple impure mineral phases, the hardening process is a complex set of different types of reactions between mineral phases. These are magnesite decarbonation, talc dehydroxylation, brucite formation and further alteration to antigorite, anhydrous silicate formation due to thermal decomposition of talc, reaction between talc and magnesite, magnesioferrite formation as alteration product of magnesite and finally, formation of Zn-rich oxides and K-rich dehydrated chlorite phase due to increments (Zn and K) from wood combustion gases. Figures 12C and 12D show positive correlations between intensifying alteration and ZnO- and K_2O-additions, respectively. The reaction sequence is not fully known. However, the Figures 9 and 11 support the findings in **Paper III** and shows that magnesite altering periclase is the only important change after 18 TSR test cycles. There is also a significant difference in microcracks, which are filled with brucite or with antigorite in the surface of the fire chamber wall rock.

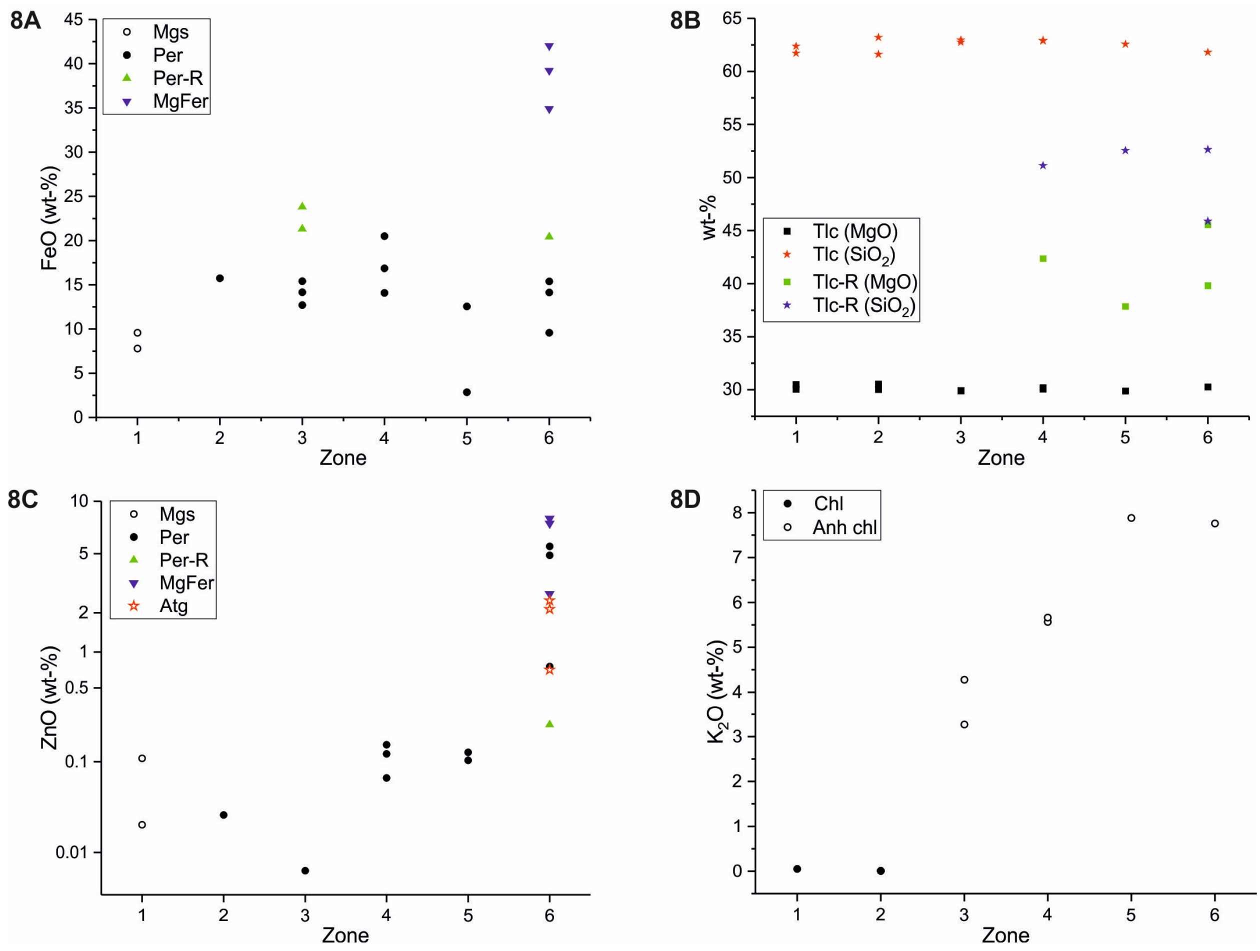

Figure 12. Distribution of most crucial metal oxides in different alteration zones in the surface of magnesite soapstone fire chamber wall rock. Anh chl = anhydrated chlorite, Atg = antigorite, Chl = chlorite, MgFer = magnesioferrite, Mgs = magnesite, Per = periclase, Per-R = periclase rim, Tlc = talc, Tlc-R = talc rim. Zone 1 (depth > 30 mm), Zone 2 (depth 30–3 mm), Zone 3 (depth 3–0.9 mm), Zone 4 (depth ~ 0.9–0.5 mm), Zone 5 (depth ~ 0.5–0.20 mm), Zone 6 (depth ~ to surface).

It is common, that pure minerals are used in ceramics and in refractory fields amongst engineered stone materials. In many occasions, it is necessary to insert some additive component to enhance the strength and durability of the product. For instance, Szczerba et al. (2013) found that MgO reacting with microsilica in 900 °C enhanced the high refractoriness of studied castables. In addition, they and Chen et al. (2016) discovered that refractory detrimental hydration of MgO can be inhibited, if microsilica is absorbed on the MgO surface. However, with the natural magnesite soapstone these artificial additions to achieve better durability, are already in place in their natural composition that formed a few billion years ago, and the fireplace user is gradually changing it into more lasting direction by keeping the fire.

6. PRACTICAL IMPLICATIONS

Regardless soapstones may consist of a wide range of different minerals, the classification of them has been generally based on their softness; practically all carvable rocks have been considered as soapstones. That is not in line with other detailed geological, e.g. plutonic and metamorphic classifications that IUGS has recommended (Streckeisen, 1976; Schmid et al., 2007). The classification and nomenclature scheme developed within this thesis is made to create a practical and concise compromise between previous classification proposals and to help geologists to speak a common language when dealing with different soapstone types. The proposal developed here fulfills both the geological void in soapstone classification and also the demand of the soapstone industry the use of different soapstone types can be optimized accurately for appropriate applications. The new classification policy would also help the consumer to acknowledge the differences between products made of different types of soapstones with distinct mineral compositions and thermal properties.

The TSR- test of natural stones was developed to have a reliable way of measuring the capacity of thermal shock resistance of different soapstone types. The method enables comparison between rock types, since each tested specimen will have a unique TSR-number, which indicates the magnitude of their capacity to resist thermal shock. The test can be used by any rock-related industry for TSR-determination. If the TSR-numbers were widely in use and marked into informative labels, they would also help the consumer to have more knowledge about the material. In addition, the manufacturers could use them as a tool to distinct their material from the products of other operators.

The mineralogical changes of magnesite soapstone exposed to high temperatures in fire chamber have been studied to understand the hardening process of the rock`s surface. The phenomenon has been known for over a hundred years, but not until this thesis, the reasons for hardening have been found. The results confirm the old observations; the composition of magnesite-soapstone surface provably hardens and it`s structure densifies. This is an essential discovery for magnesite soapstone fireplace manufacturers, since they can rely on functionality of magnesite soapstone with suitable structure in high-temperature applications such as in fire chambers and in funnels. The hardening process takes place gradually along the fireplace use over time, hence the artificial materials are not needed to cover the natural rocks in fire chambers. Manufacturers can benefit by fewer workload in production and by using only natural material, which maintains its excellent thermal properties in high-temperature use. This thesis answers some of the key-questions regarding the durability of magnesite soapstone required in high-temperature applications.

Overall, the findings in this thesis provide new information for soapstone industry to utilize the natural benefits of magnesite soapstone, which serves high-quality material for residential heating and other high-temperature applications, if selected with care. By using appropriate soapstone type as fireplace material, extremely high temperatures can be employed. This leads to more particulate free combustion. As a construction material of capacitive fireplaces, magnesite soapstone can reserve heat efficiently and slowly release it, decreasing the need of firewood quantity.

7. RECOMMENDATION FOR FURTHER RESEARCH

The final test runs developing the new thermal shock resistance test were carried out along with this thesis. The test method has been proved to give accurate information about thermal shock resistance of different soapstone types. The TSR-numbers provided the test are unequivocal and comparable to each other. The aim is to standardize the test in the near future.

The significance of zinc and potassium additions from wood combustion gases are not fully understood. Is magnesite soapstone the only fire chamber construction material that binds those components to itself? In which time the hardening of magnesite soapstone surface occurs in fire chamber constructions? Reaction modellings and further studies of microstructure of fire chamber wall rocks regarding the gas discharge are also needed. Finally, awareness of the developed soapstone classification should be promoted in both academic and industrial sectors at international level to receive wider attention and acceptance.

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