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## II International Workshop on Heritage Stones

Torino (Italy), 5<sup>th</sup>-7<sup>th</sup> October 2021



### Study for Supporting Restoration Activities of Rapakivi Granite in St.Petersburg

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#### Summary

The paper addresses the background, challenges and opportunities provided by restoration needs of built cultural heritage of St. Petersburg. NaStA project (*History and Future of Natural Stones in Architecture – Bridge Between South East Finland and Russia*) focus on methodologies based on a demand for conservation and in a specificity for substitution of detached fragments. The focus is on two rapakivi granites, wiborgite and pyterlite, that have been used in St Peterburg since 1760s but originate from southeaster Finland. Prominence of this research has been on defining the original quarries of the old building stones or finding the other similar substituting granite deposits. Chemical information measured with handheld XRF instrument were found most promising approach when interpreted with multivariate mathematical tools. In addition, applicability of chemical treatment of on surface of rapakivi granite were studied to change appearance of stones and rocks. Visual appearance and texture of natural stones in conservation are the major factors in addition to stone type and quality. In addition, the project activities include creation of databases for stones utilized in historical buildings and for relevant quarries located in NW Russia and SE Finland as sources of original or alternative granite substitutes. Moreover, the project activity supports establishment of a network to overcome the issues connected to the cross-border trade and national legislations.

#### Introduction

The research has been driven by the needs for restoration of stone constructions in St. Petersburg, Russian Federation. The peculiarity stands in the fact that large part of the material applied in the historical centre of St. Petersburg, listed in the UNESCO World Heritage list, has nowadays Finnish provenience. Even though the project collects information from several stone types historically used, this study is focused on a specific granite quarried on the border with Russia, on the southeast regions of Finland: Rapakivi granite and its economic and social relevance for the area along the years.

#### Material under study

Southeast Finland has been long known for the production of rapakivi granite. The material is used worldwide, and it has been the main source for the construction of St. Petersburg in North West Russia in the 17<sup>th</sup> – 18<sup>th</sup> century. Rapakivi granite of different qualities can be seen in many famous buildings and constructions in the historical centre on the city as the Embankments of Neva River, the pillars of Isaac's Cathedral and the monolith in the monument of Tsar Alexander (Bulakh 2000, Bulakh et al. 2010, Bulakh A. G. et al. 2020).

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Figure 1. On the left a view of the interiors of Isaac's Cathedral and on the right the view of the monument of Tsar Alexander. Photo: Mika Räisänen

### Geological setting:

The Proterozoic rapakivi granites of Finland are found as four major batholiths of which the Wiborg rapakivi granite batholith locates in southeaster Finland. It covers an area of approx. 18 000 km<sup>2</sup> and the age of the batholith is 1635–1628 Ma. The batholith extends to NW Russia in the east and beneath the Gulf of Finland in the south. Seven main types of rapakivi granite were determined in the Wiborg batholith comprising wiborgite, dark wiborgite, pyterlite, porphyritic rapakivi granite, even-grained rapakivi granite, dark rapakivi granite and aplitic rapakivi granite. The abundances of the different rapakivi types of the batholith on the Finnish side are: wiborgite 75%, pyterlite 6%, even-grained rapakivi granites 6%, dark rapakivi granites 6% and other types 7% (Härmä & Selonen 2018, Härmä 2020). Wiborgite has a typical rapakivi texture with K-feldspar megacrysts (ovoids), size of 1–4 cm on average, mantled by a plagioclase rim (Figure 2A). The main colours of the wiborgite are brown and reddish brown. The main minerals are K-feldspar, quartz, plagioclase, biotite, and hornblende (Härmä 2020). Pyterlite is a red coloured rapakivi granite variety with rounded K-feldspar megacrysts 1–4 cm in diameter in medium-grained matrix, but megacrysts lack the rim of plagioclase (Figure 2B). The main minerals are K-feldspar, quartz, plagioclase, and biotite (Härmä 2020). Pyterlite and wiborgite are the two main rapakivi granite types applied in historical buildings of St Petersburg

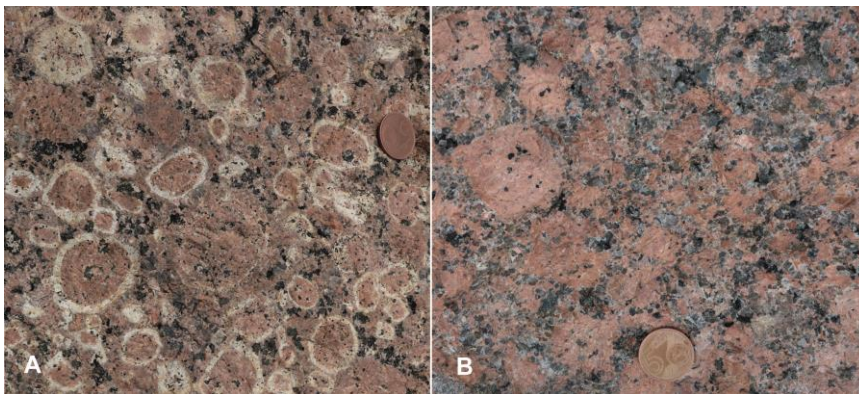


Figure 2. A. Typical wiborgite and B. pyterlite. Ellipsoidal megacrysts (ovoids) are 1–4 cm in diameter and lack the rim of plagioclase in pyterlite. The coin is ca 2 cm in diameter. Photo: Paavo Härmä.

### Successful production area in the past and in the present

The main production areas are located to the southeast border of Finland in modern days. It has been an area that shifted governance between Swedish and Russians before Finland gained full independence thus it has been affected in its development by the border conflicts. In 1788–1800 the area has seen massive fortification to protect St. Petersburg. Under Russian domination the fortresses of Ruotsinsalmi, Kyminlinna, Hamina, Lappeenranta have been built using mainly locally extracted rocks, that are rapakivi granites. (Paajanen 2014).

While Swedish domination has been detrimental for the local economy, the era as autonomous Grand Duchy of Finland that followed (1809-1917), favoured economic and social development. In 1917 Finland

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If this is the history about granite production and export then some numbers or estimates over the time would be really interesting – there is some at the end, but all this history of quarries?



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declared independence and the economy grew relatively quickly and new economic relations developed also with Soviet Union/Russia. Nowadays namely Leningrad Oblast and St. Petersburg are the most important trade regions in Russia to Finnish enterprises.

In 19<sup>th</sup> century the area of Virolahti (Fig3.), where historical quarrying took place, quite doubled in population, reaching 10.000 inhabitants in 1887. The history of quarrying and utilization of red rapakivi granite in the area started already in the 18th century. The first extractive site was Käräsän quarry of the village of Koskela in 1650 (Raunio E., 1965). Stone production determined wealth, because it employed personnel and complementary services as transportation, accommodation, catering, maintenance, health, and education.

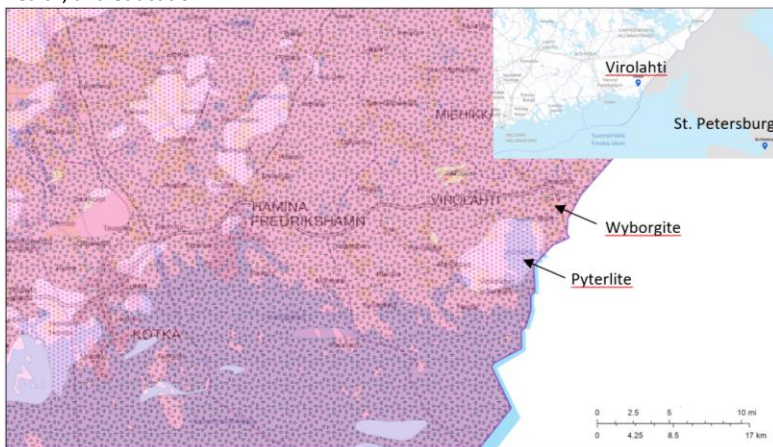


Figure 3. Area of Virolahti and the vicinity to St. Petersburg. Bedrock map showing the rapakivi area in pink. Wyborgite and Pyterlite areas are highlighted. (Bedrock Map copyright GTK 2019, Land map printed by Land Survey of Finland)

Besides for fortifications, the main stone need has come for the construction of St. Petersburg that has been founded in 1703 during Tsar Peter I (1682-1725) under design of important European architects. Until 1918 acted as the capital of the Russian territory.

Natural stones were used for paving streets (setts, cobbles and kerbs), structural and decorative elements in buildings. The rapakivi granite is suited for all interior and outdoor uses and it plays an important role because of its durability and hardness. The quality, material availability, the workability, colour and technical properties made the red rapakivi a favourite stone in the construction of the city.

The quarried area was within Russian territory at the time, it was near St. Petersburg, and it was easily accessible. In the past, the water way has been the key to commercial development for the region and, in this case, allowed movement of heavy and dimensionally problematic loads as the 48 rapakivi columns for the Isaac's Cathedral and the monolith for the monument of Tsar Alexander. The architect August de Montferand pictured the techniques adopted to shift the loads to the boats and the accidents occurred when he was supervising the works in early 1800. (Kaukiainen, Y. 2016)



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The quarry of Pyterlahti in Virolahti was producing granite for the Russian market and Laitaka reported that up to three thousand workers, often prisoners have been employed (Laitaka A. 1954). It is not known when there has been a shift from prisoners work to private enterprises, but it is reported that in early 1800 the first Russian private companies started to be operative, employing mostly Russians, while the first Finnish started to work from 1850 (Raunio E. 1965). Pyterlahti is the quarry that originated the monolith for the column of Tsar Alexander. The biggest quarried monolith was told to wait 360 tons (Laitaka A. 1954).

Much is learned from Montferrand's description about extraction and transportation of the columns, where thousands of people have been used to move the monoliths. (Kaukiainen, Y. 2016). Technically the utensils and technology adopted, that varied from material extracted, has been first documented in the Encyclopédie of Denis Diderot and Rond d'Alembert (1751-1772). Standard wedge and, in the 18<sup>th</sup> century, hand drilling have been the main technologies in use, and signs of the work might still be visible on the blocks on the building and on the historical quarry sites. The hand splitting required tools and capacity. (Kaukiainen, Y. 2016, Laulumaa V, Väisänen T. 2017)

A bookkeeping from the Finnish Stone Workers' Association, Suomen Kivityöntekijän liitto, reports from early 1900 that workers could either own the equipment facing maintenance costs or could use the equipment provided by the extractive company. The payment was based on finished product delivered; thus, it was relevant the ability of the worker in the earning. Stone is a tricky material, being natural, could hide fractures and irregularities that come visible only while manufacturing the objects and for a long time the expertise of the stone manufacturer determined the success of the production not only in the technique applied but also in the evaluation of soundness of the material (Suomen Kivityöntekijän liitto, 1923). The quarry of Pyterlahti has been used because of the quality of the material, adequate for production of monuments that required massive, faultless, sound blocks. (Laitaka A. 1954) In late 1800 and early 1900 is also told that women could have an active role in quarry production, having for example the duty to fix the peaks after the block has been detached from the bedrock, and before it would be moved by rolling. (Raunio E. 1965)

Virolahti area has over 200 years of history in quarrying. During this time 43 quarries have been operational, spanning over a 45 ha area and exporting 1million m<sup>3</sup> of stone. The last export from the area happened in 1925. (Raunio E. 1965, Kaukiainen 2016)

The count of the production performed in the historical period of operation of the quarries, that lasted over 200 years, in the area of Virolahti shows that have been dedicated to extractive activity over 45 ha of land by 43 quarries, it has been exported 1million m<sup>3</sup> of stone, and have been used 160 docks with a complex length reaching 3,5km. From the territory over the actual border have been quarried 58ha, and exported 116.600m<sup>3</sup> of stone. The last export from the area happened in 1925. (Raunio E. 1965, Kaukiainen 2016)

The rapakivi production grew again after the world wars even leading for some times the world granite export. Today Finnish rapakivi commercially produced in the South East Finland regions are Carmen Red, Baltic brown, Baltic green, Eagle red, Myrskylä red, Kymen brown and Kymen red, Karelia beige.

The Finnish companies mainly export rough blocks and the market has been worldwide, with a small rate to Russia. The export of "granite roughly cut products" to Russian Federation has been varying according to the Uljas - Statistical Database, with a boom in the years 2011-2013 lowering in years 2015-2016 and

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growing in years 2017-2018. The scale of revenue reached half a million €/year and the destination are mainly for constructions in Moscow and St. Petersburg (Männikkö J. 2021)

The trade between Finland and Russia is strongly regulated by complex administrative documentation, even though the stone trade in this sector is mainly focused on exporting raw blocks to be manufactured into final products in Russia. The stone from Finland can access Russian territory only with a predefined Russian Federation registered entity acting as importer. Sales contract, Invoice and Pro forma, Customs declaration and declaration of dutiable value in Russian, Documents of export, Certificate of Origin, Consignment note, Certification and conformity certificate, Declaration of conformity, certificate of Quality, Radiation free certificate, Hygiene certificate are documents needed to export to Russian market and that can either be provided in English/Russian. Some certificates should be reported by accredited laboratories according to Russian federation's standards even if practice allows testing done according to Finnish regulation by Finnish authorities. (Luodes N., Luodes H. 2014) Control on track weigh performed according to different procedures in Russia and Finland requires special preventive measures to allow smooth border crossing. The maximum weight should be 24.8 tons and lack of uniform regulation can cause delay at the border.

Nowadays stone trade towards Russia happens mainly on wheels, even if train transport is well developed and access to inland water and open sea is also in the vicinity.

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In Russian Federation the costs of imported material compared to local is about triple, making the imported material a symbol of wealth. As discussed, the demand has not been constant. Recent EU sanctions towards Russia diminished even further the export from Finland towards Russia, where grew stronger the use of local material. In general stone accounts for about 7% of the construction materials used, with the largest share of slabs and tiles. (L Männikkö J. 2021) Stone's durability is higher compared to other materials, its production life cycle 's environmental impact, compared to cement and ceramic production, is low, making it a green material. An analysis of the carbon footprint for Finnish stone industry has shown that the emission varies between 15-35 kg/CO<sub>2</sub>/m<sup>2</sup> according to level of manufacturing reached. Highest emission corresponds to countertops, while lowest to kerbs. **Rough blocks have the smallest carbon footprint as it is not yet performed further the manufacturing.** Transportation is also affecting the carbon footprint, therefore it is preferable to have local production to drop the emissions (Kivi Ry., 2020) St. Petersburg has high reachability on the coast and short distances to Finnish border producers.

Nowadays, Finnish companies, operative in the rapakivi area, export to Russia mainly rough blocks that have a lower value compared to the finished products, and transportation costs become important in the calculation of the net income. Best results come with large procurements, having the stone producers using a Russian trusted logistic partner with whom is important to establish long term cooperation to ensure continuity of the service. (Männikkö J. 2021)

When thinking of material that would be used for restoration the quantities are small but the quality and accuracy in surface preparation give each piece a higher value.

### Needs and Conservation

"Historic Centre of Saint Petersburg and Related Groups of Monuments" became the first Russian site to the UNESCO World Heritage list in 1990 and it is mainly built with stone. Several maintenance works have already been realized. Construction made of granite also needed reparations, even though the granites have a high durability compared to other rocks. In the coastal Nordic city environment, granite



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experiences various physical, chemical, and biogenic weathering. Durability of Nordic granites as construction material has been researched along the years. Typologies of weathering have been addressed through multiple studies and have been extensively illustrated by Panova et. al. 2014. Field evaluation of conservation state of the buildings have showed that granites displayed mechanical damages, depositions including biogenic growth, stone losses. Under a simplified perspective, the mechanisms of weathering identified have been the freeze thaw cycles during the autumn and spring, the salt environment by the vicinity of the sea, and the pollution levels undergone during the past years. (Panova et. al. 2014, Frank-Kamenetskaya, 2019) This has been more intense in St Peterburg compared to the coastal area in Finnish territory.

Often, the old stone shows a patina, that can be a crust or a surface layer. This might be appreciated on the historical object. (Delgado Rodrigues, 2006). Sometimes the weathering actions can impact the stone to such an extent that fragment start detaching, and conservation action need substitution of the material (Fig 4).

AB

CD

*Figure 4. Biogenic growth, detachments, crust deposition visible from stone buildings in the Finnish and Russian coastal environment. Photos A,B Nike Luodes, (depositions and detachments - Helsinki), Photos C,D Mika Räsänen (detachments - St.Petersburg)*

In 19<sup>th</sup> and 20<sup>th</sup> centuries several conservation theories have developed. Preservation, restoration, reconstruction and adaptation measures and their combination range from causing lowest impacts on the manufact up to substitutions. These are suitable for different sites, respond to specific heritage policies and pursue different goals. The concept of conservation has developed to allow adaptive reuse, maintaining the significance of the site while using it for contemporary needs. (Mehr S. Y. 2019, Rouhi J 2016)

Cultural heritage conservation policies in Finland include Act on the Protection of the Built Heritage (498/2010) (<https://www.finlex.fi/fi/laki/ajantasa/2010/20100498> ) and ratified European and world conventions (Council of Europe Faro Convention on the Value of Heritage for Society, Unesco Convention on the Safeguarding of the Intangible Cultural Heritage, and the Unesco World Heritage Convention). The Centre for Economic Development, Transport and the Environment and the Finnish Heritage agency are the authorities.

Russian Heritage Institute under Russia Ministry of Culture of the Russian Federation is the reference authority in Russia. The main law on built environment is the [Law on Objects of Cultural Heritage of Peoples of Russia](#), (Law 73-FZ). National cultural heritage laws are collected into UNESCO database <https://en.unesco.org/cultnatlaws>. In both countries exist cultural heritage register collecting the sites that are under protection. These are based on historical documentation and generally describes the constructions. It usually not specifies the material and its origin, mainly when addressing stone architectural objects.

### Tools for conservation

Detachments of fragments can occur on the construction. These can be caused by mechanical impacts or by weathering. Substitution during renovation activities means the placement of fresh material in the place of detached one. Substitution might impact visually the cultural heritage and if replacement material

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differs in properties, structural performance might be affected. The old construction stones have undergone some levels of weathering and might present a patina while the new stone, even if of original provenience, might differ in appearance impacting on the harmony of the built environment. It is in some cases wished to reproduce the surface patina on the fresh stone, so that it can visually melt with the older ones. In some cases, the extraction site of the original stone might not be known or exist anymore, and alternative stones have to be chosen. The choice and surface treatment of the material is a critical step in the process of substitution of architectural elements (Fig 5).



Figure 5. A. Channel embankment, in the centre of the embankment is visible the substitution of original material, rapakivi granite, with different stone type, limestone. Photo: Heikki Pirinen. B. Restoration of the lower part of pillar using same rock type as original at Cathedral of St Isaac. Photo: Mika Räsänen.

In order to support the selection of the substitution stone, NaStA project (Figure 6) collects data of stones utilized in historical buildings and data of original and alternative quarries, develop tools for supporting the experts in the identifications of potential stones and research surface treatment of new stone products to gain proper appearance that could be used by the industry. The project then organizes clustering events to connect possible material providers with manufacturers to meet the needs of the authorities. As seen previously, a trusted network of partners facilitates the trade.



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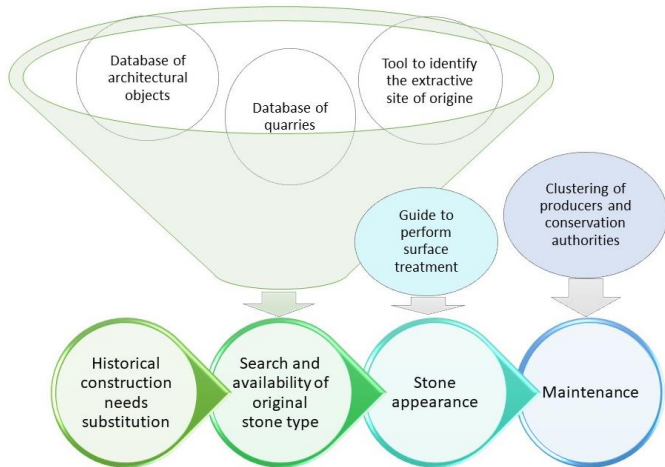


Figure 6. Schematic visualization of the approach developed in NaStA project for substitution stone process.

Tools aiming to aid benchmark correct substitution materials are developed; database linking restoration materials and their sources, tool for identification of potential substitutes, and procedures for changing visual appearance in manufacturing process.

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### Collection and availability of knowledge

At best, the restoration is done by using the same skilfully crafted stones in place of the original stones (Figure 5B). It is also important to produce and store authentic restoration stone materials in order to be able to maintain the restoration activities in the long run, and to preserve the cultural heritage. In course of NaStA two open databases are created; a database of the stones applied on construction (1) and a database of historical quarries of the region (2). The first database of objects and rocks include more than 300 constructions of St Petersburg and South East Finland. It defines the location and short history of the manufacture and lists the stones used in each architectural element and their quarry of origin. The second database of quarries and rocks covers the historical quarries mapped during the project. These databases contain among others technical properties of the stone, when available, and both the historical and modern name of the stone. When the material on the building is known and information on material availability is collected, the experts can utilize the information when selecting the restoration material. The database is open and accessible to authorities as well as to entrepreneurs.

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### Overcoming challenges in determination of the quarry of origin

When planning a substitution, it is preferred to use original material but the identification of the historical quarry of origin might be a challenge. It is performed bibliographical research from historical records, but, as noticed during the development of the database, even if information relative to the construction is found, those about the procurement of the stone are missing. For this reason, during the project is developed a tool to identify the extractive site of origin.





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Chemical information of stones could be utilized to trace the original quarry sites, or sites that have similar stone for substitution. Data types applied can be divided in 1) chemical elemental data (e.g., ICP-MS, or XRF) or 2) spectroscopic data (FT-IR, Raman, hyperspectra). Special requirement for the choice of the equipment is the ability to measure *in-situ*, and be non-destructive. Feasibility of tree handheld instruments were evaluated in the present project. The laboratory instruments require extraction of samples to be transported to the laboratory. The main instrumentation applied developing the procedures for identification and surface analysis are described in Table 1.

Table 1 Main chemical instruments applied in NaStA project in identification and feature studies of granite samples.

Abbreviation	Name	Instrument type	Data description
XRF	X-ray fluorescence spectroscopy	Portable, handheld	Concentration of over 30 chemical elements
FT-IR	Fourier Transform Infrared	Portable, handheld	Spectra typical for certain material
Raman	Raman spectroscopy	Laboratory instrument	Spectra typical for certain material, spectral library for revealing mineral
Hyperspectra	Hyperspectral camera	Portable, handheld	Electromagnetic spectra in visible region
ICP-MS	Inductively coupled plasma mass spectrometry	Laboratory instrument	Concentration of over 25 chemical elements from liquid samples
SEM	scanning electron microscopy	Laboratory instrument	Images from surface structure
EDS	Energy-dispersive X-ray spectroscopy	Laboratory instrument	Chemical composition from SEM images

The mathematical tool developed can apply various chemical or physical data to identify the origin or similarity between the target and substitutive stone. The basic methodology follows *Soft independent modelling by class analogy* (SIMCA) where *Principal Component* (PCA) models are utilized to extract information from data describing the stone or rock material. The potential substitution stones are measured and compared to the original stone. PCA model(s) capture systematic variation, e.g., ratios of chemical compounds, or spectra specific for the stone. The similarity is described and identified with various indicators that upgrade the original SIMCA methodology (Kowalski et al, 1977). Applicability of SIMCA with the extended alternative classification indicators have been evaluated with case studies. Results of case studies and concept of the novel fingerprinting tool will be published and discussed in project results. Nash et. al has recently applied PCA based methodology to chemical composition data to reveal origin of the stones used to build the monument of Stonehenge (Nash et al, 2010).

### Overcoming challenges in the manufacturing of a substitute material

When the origin of the stone is defined, is to be evaluated the feasibility of the extractive activity. Historical extractive site might not exist anymore, or it might not be exploitable being too closed to residential areas and under a different land use denomination. An alternative substitution stone must be found, and it should be as similar as possible to the original one.

Visual appearance is a critical issue, when assessing the match between original building stone and a possible substitute. However, colour of natural stone is not uniform, and patterns and texture on surface have most significant role in construction stones. Photogrammetric methods provide a way to compare

**Добавлено примечание ([SPR10]):** Zina-Sabrina Duma, Paavo Härmä, Heidi Laxström, Tuomas Sihvonen, Aleksi Surakka, Satu-Pia Reinikainen, Tool for Building Stone Similarity Identification: A Case Study of Rapakivi Granite from Kotka Area, Finland, Geotechnical and Geological Engineering, 2021 (submitted)



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the colours and patterns of the stones. These methods do require advanced arrangements for example to correct differences in lighting conditions between images. Researchers have proposed various procedures to measure and compare the colour of granite samples. Pireto et.al. studied the colour of granite stones by colorimeters (Prieto 2010). They found that repeated measurement over a surface area gives a good representation of the stone colour. Thornbush has calibrated digital photos by a grey card and compared the results against a colorimeter (Thornbush 2008). He found high correlation with the white balanced pictures and the colorimeter, indicating that calibrated colour photos could be used to study the change in the stone colour. These techniques are useful also to compare the treated stone against the fresh material, and the fresh and treated stone against the site historical stone. In the present study authors applied colour standard card and typical photometric set up in laboratory, when comparing colours and their histograms in samples.

When a substitute rock type, similar in properties and in typology is chosen, surface appearance might still deviate from the material on building site, that has developed a patina. Therefore, procedures adequate for industrial manufacturing or artisanal production to modify the surface appearance are critical. In the NaStA project, one objective is investigation of novel chemical and thermal surface treatments of pyterlite and wiborgite rapakivi granite.

The procedures contemplate several combinations of thermal and chemical surface treatment of the stone samples. The thermal treatment was performed at 300-600 °C oven with varying exposure time. The chemical treatment steps occurred before and after the thermal treatment. The mechanisms attempted were oxidation, ion exchange and other chemical reactions. As a results, the dark and black pattern from surface typically decreased, and reddish or brownish surface area increased and changed the colour tone. Table 2 and Figures 7 and 8 illustrate an example. Similar phenomenon was found in Wiborgite and Pyterlite samples. Acidic treatment were performed with for example phosphoric acid (2 mol/L). The treatments caused changes in certain minerals as shown in the figures. Visually the dark fraction decreased and red fraction increased. Specific result to phosphoric treatment in Wybergite was the increase of white-light fraction. In table 2 are listed the changes in visual appearance caused by the treatments.

*Table 2 Change in surface area captured by the tree colour tones in Wiborg and Pyterlite samples in thermal treatment and acidic treatment. Sample surface was classified in three categories according to the colour tone.*

Sample description	Red or brown	Dark or black	Light or white
Wiborgite, original with 95 % confidence area	66 % ± 2 %	29 % ± 1 %	4 % ± 1 %
Wiborgite, thermal treated	89 %	10 %	1 %
Wiborgite, phosphoric acid treated	74 %	20 %	6 %
Pyterlite, original with 95 % confidence area	64 % ± 4 %	36 % ± 4 %	0 % ± 1 %
Pyterlite, thermal treated	97 %	0.3 %	3 %
Pyterlite, phosphoric acid treated	75 %	23 %	1 %

The treated wiborgite and pyterlite samples are presented in Figures 7 and 8. Photos of the samples treated have been taken with a high-quality digital camera. An obstacle (granite sample) was set on a stand under chosen photogrammetric set-up, and a colour standard grid placed near the obstacle as reference. Colours of photos were corrected to correspond the known this colour standard. On the figures the main minerals visible at naked eye are marked.



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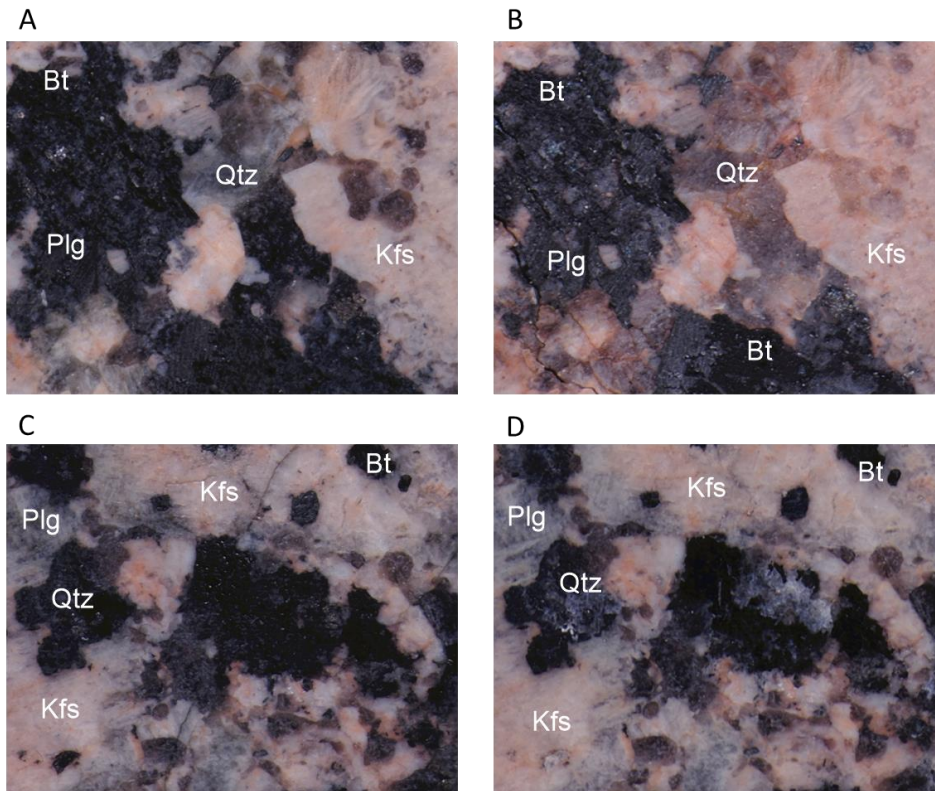


Figure 7. Wiborgite sample A) original sample before, and B) after thermal treatment in 600 °C. C) original samples before, and D) after phosphoric acid treatment. Abbreviations of minerals in the figure: Kfs = K-feldspar, Qtz = Quartz, Plg = Plagioclase and Bt = Biotite.

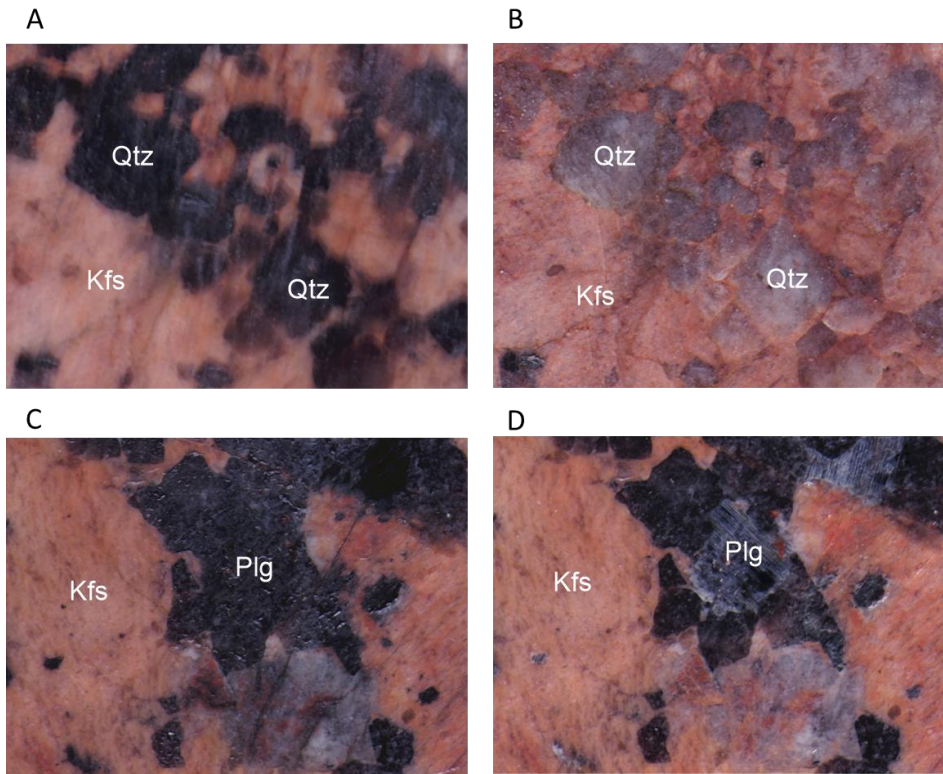


Figure 8. Pyterlite sample A) original sample before, and B) after thermal treatment in 600 °C. C) original samples before, and D) after phosphoric acid treatment. Abbreviations of minerals in the figure: Kfs = K-feldspar, Qtz = Quartz, Plg = Plagioclase.

In addition, the changes on surface structures were analysed with scanning electron microscope (SEM), and optic microscopes. Chemical compounds were identified with EDS, FT-IR, Raman, XRF spectroscopy and ICP-MS (Table 2). Handheld XRF was the main instrument applied to illustrate the change in concentration of chemical compounds. Total 35 elements were measured. Number of measurements from each stone sample varied from 10 to 99. Table 3 shows results from pyterlite and wiborgite samples; original sample before treatment (n = 50-99 measurements), and samples after (n = 10-20) the treatments with phosphoric acid or heat.

Table 3 Concentrations of 11 chemical compounds from surface treatment experiments. Number of measurements, n, vary between 10-99. Treated samples n = 10 times. Expanded 95 % uncertainty range presented for original values.

	Wiborgite, Baltic Brown	Pyterlite, Carmen Red
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Main compounds	Original (n = 99)	Thermal Treated	Acid Treated	Original (n = 50)	Thermal Treated	Acid Treated
Al, mg/kg	67552± 3596	45346	83507	57523 ± 3065	79051	46170
Ca, mg/kg	10954 ± 1034	15977	8358	4248 ± 401	5002	3221
Fe, mg/kg	27023 ± 4345	78063	7265	8964 ± 1441	5618	21333
K, mg/kg	44846 ± 3366	34678	59642	46754 ± 3509	68726	40941
Mg, mg/kg	1539 ± 269	3525	1177	1236 ± 216	1081	1043
Mn, mg/kg	393 ± 54	1080	171	147 ± 20	125	252
P, mg/kg	393 ± 106	1420	1875	156 ± 42	27	5749
S, mg/kg	50 ± 13	4526	35	34 ± 9	623	32
Si, mg/kg	309921 ± 4935	276213	304320	346694 ± 5520	313198	356396
Sr, mg/kg	139 ± 2	91	178	76 ± 1	101	62
Ti, mg/kg	3960 ± 599	12420	2259	1416 ± 214	1016	2443

The XRF instrument has analytical limitation. The absorption of X-rays by air prohibits the measurement of lighter chemical compounds than magnesium (for example Na cannot be determined) (Demistar et al. 2020). Also, the Mg results presented have very high uncertainty, and the concentrations tend to be under detection limit (sample dependent, approximately 3 g/kg) in most rapakivi granite samples. In contrary concentrations of e.g. Si, Al, and K could be determined with 2-5 % extended uncertainty range. Low uncertainty is due to homogeneity of surface and low analytical error. Pyterlite and Wiborgite samples had very similar K and Si concentrations. Results suggest that Si concentration is not affected in acid treatment, but thermal treatment decreases it by 10 %. FT-IR spectra revealed changes in silica compounds.

Thermal treatment in 600 °C did increase the red/brown surface from 65 % to 89-97 %, and dark areas (plagioclase or quartz) were covered with thin opaque white layers. XRF results revealed minor decrease in Si compounds. In case of Wiborgite the Fe, Mn, (Mg), P, S, and Ti concentrations increased, and Al, K, and Sr compounds disappeared. Pyterlite got even stronger white layer to the dark quartz areas, and in XRF analysis Al, Ca, K, and S- concentrations increased. The increase of sulphur was very clear in both cases. In Pyterlite case Fe, (Mg), P and Ti compounds decreased in the surface. Further studies with other instruments can reveal the real phenomena and composition behind these results.

Treatment with 2 mol/L phosphoric acid increased amount of phosphoric compounds in surface. In case of Wiborgite it decreased occurrence of S, Ca, Fe, Mn, (Mg), and Ti compounds, while Al, K, and P compounds increased. Acid had dissolved compounds from surface, and exposed Al and K containing minerals (e.g., K feldspar). New phosphorous compounds had formed. In case of pyterlite acidic treatment decreased Al, Ca, K, and (Mg) concentrations and increased presence of Fe, Mn, P, and Ti. The result showed a clear difference in phenomena caused in chemical composition in the two cases. In both Rapakivi granites about 65 % of the surface was originally reddish/brownish feldspars that increased to 75 % in acidic treatment. The K nor Si occurrence did not change, but the visual appearance of dark areas (plagioclase and quartz) changed, and white or light compounds appeared to surface layer, hiding the dark colours.

Surface treatment methodology is further elaborated within the feasibility study considering several technical and economic aspects.



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### Entering the market

When the stone is manufactured, before entering the market, undergoes characterization and quality tests. When addressing modern constructions, stone products are tested according to the national standards. Table 4 lists the product standard of reference for Russian and EU markets. The European standards listed are those that allow the application of the CE label.

Table 4 Lists the product standard of reference for Russian and EU markets.

GOST 30629 – 2011 “Facing materials and items made of rocks: testing methods”	EN 1341 Slabs of natural stone for external paving – Requirements and test methods
GOST 23342 – 91 Architectural-building items made of natural stone. Technical conditions. (ref. EN 1467- Natural stone - Rough blocks - Requirements).	EN 1342 Setts of natural stone for external paving – Requirements and test methods
GOST 9479 - 2011 “Rock blocks for production of facing, architectural – building, memorial and other items” (ref. EN 1467- Natural stone - Rough blocks - Requirements)	EN 1343 Kerbs of natural stone for external paving – Requirements and test methods
GOST 9480 – 89 Facing slabs sown from natural stone. Technical specifications. (Ref.GOST 9479)	EN 1469 Natural stone products - Slabs for cladding - Requirements
GOST 24099-80. Decorative plates on the basis of natural stone. Specifications.	EN 12057 Natural stone products - Modular tiles - Requirements
GOST 30629-99. Facing materials and products from rocks. Test methods.	EN 12058 Natural stone products - Slabs for floors and stairs - Requirements
GOST 9479-84 Physical and mechanical properties	EN 12326-1 Slate and stone products for discontinuous roofing and cladding - Part 1: product
	EN 12326-2 Slate and stone products for discontinuous roofing and cladding - Part 2: methods of test
	EN 771-6 Specification for masonry units - Part 6: Natural stone masonry units

Generally the GOST and EN standards differ in classifying a product. Classes of products are lower in the GOST standards. Still, in order to overcome the barriers caused by product certification, some GOST standards started to be developed taking into account the European standard for similar property or product, as visible in the table 4. It is rather important that tests are performed according to the same standard because change in testing methodology also determines differences in the results and uncertainties in evaluation of the properties of the stone.

When all the knowledge relevant to productization of a substitute for renovation purpose is collected, trade cannot happen without suitable contacts. As seen previously, for trading material to Russia, a national contact importing the material has to exist, and trading happen smoothly when a trusted and established network is operative.

The last activity of the project is to create possibilities for establishing first contacts between the authorities that are in charge of the cultural heritage conservation, the construction companies that have



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to perform the work of renovation, the stone producers that provide the original or substitute material and the manufacturer that produce the needed high quality pieces. Clustering events, even in remote, are a tool to exchange information and create new contacts.

### Conclusions

The knowledge built in the project activity is fundamental to increase the cross-border trade possibilities when answering to conservation needs. It supplies extensive knowledge on the material applied on the construction and their origin in an extensive database that cover NW Russia and SE Finland. Knowledge is normally difficult to obtain only from bibliographical research. The research provides mathematical tools for identification of origin and similarity of stones, and chemical surface treatment procedures for manufactures. The first results of the project are here shown but the aim is to support in productization of suitable substitute for conservation activities. The trade between Russia and Finland presents several bottlenecks and cross border cooperation between involved stakeholders as well establishment of trusted cooperation is essential to promote trade.

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**Keywords:** natural stone, rapakivi granite, surface treatment, fingerprinting, South East Finland, St. Petersburg

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