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# CaO- MgO-glaze for cordierite clay body

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**Abstract**. In Finland there occurs magnesium containing saw-waste as a by-product from soapstone industry included talc minerals, which can be used for manufacturing of cordierite clay body. In this work properties and raw materials, which are needed for glazes used to cover the magnesium silica clay body, have been investigated and evaluated. With Finnish whiting, dolomite and feldspar FFF as raw materials also the phlogopite mica, a by-product from apatite mine, has been used as a glaze. The limited industry production can withstand some variations and thus utilize natural rock minerals which also colour the glazes. The glazes have a high viscosity and a good covering effect. Colours have a brownish beige or yellow tone from iron oxide when magnesium and calcium oxide are used together. The surfaces of the glazes, which are developed in this investigation, can be used both for tableware design, which withstands chock temperatures and in applications for illustrious tile surfaces in the tile industry.

## Introduction

The cordierite used in the glaze investigations contains soapstone sawdust residues from mining in North Carelian. High ironed soapstone is not a problem waste and not disadvantageous for the environment. In this investigation it is used in the manufacture of the cordierite clay. Without additional milling it has an enough fine particle size to be used in amounts of 20 - 60 w-% [1]. It is easily wetted and is better mixed with water than talc. In the village Nunnanlahti in North Carelian, in Finland the soapstone has the following mineral composition: Talc, $Mg_3Si_4O_{10}(OH)_2$40 - 50%, Manganese, $MgCO_3$ 40 - 50%, and including Chlorite, $(Mg, Fe)_5$ $Al(Si_3)Al)$ $O_{10}$ $(OH)_8$. During firing the natural raw material changes the colour of cordierite from grey to brown depending on the amounts, which are used. Cordierite clays are used to make household ceramic tableware resistant to cooking thermal shock and also for fire clay bricks and tiles in the building industry. The formation of glazes on the clay bodies containing magnesium oxide differs from the formation of common clay bodies [2].

In the present investigation the composition of glazes on the surface of clay bodies containing soapstone is investigated. The properties of the glazes used together with clay bodies containing soapstone should be similar to those used with the cordierite pulp. As a cordierite raw material soapstone powder, ball clay Hyplas 64 (ECCI), china clay Standard porcelain (ECCI), Quartz FFQ are used. The chemical analysis of the cordierite clay body used in the testing of glazes is: $SiO_2$ 67.541, $Al_2O_3$ 18.014, $Fe_2O_3$ 0.538, $TiO_2$ 0.544, CaO 0.849, MgO 11.225, $K_2O$ 1.291 w-%. The cordierite is sintering when fired over 1200°C in an oxidation atmosphere in an electric kiln. During the temperature 1200-1240°C cordierite containing soapstone sintered rapidly within a very short range when the firing rate is 100°C/h. The maximum soaking time used is 20 min. The aim is to develop a glaze with high magnesium content and which act as a thin glaze on the surface of the cordierite clay body.

## Glazes

**Raw materials.** The selected raw materials for the glazes are: Standard porcelain china clay (5-10 w-%), Finnish Flotation Feldspar FFF (25-45 w-%), Quartz FFQ (20-45 w-%), dolomite (5-22 w-%) and whiting (20-30 w-%) and the more seldom used phlogopite mica (10-30 w-%)[3]. Phlogopite mica is by-product from Apatite Mining Company in Siilinjärvi. Phlogopite mica contains magnesium oxide, which was the reason for its selection in the testing of glazes. In the glazes two frits from England, Pottery crafts frits P2953 (potash and calcium boron silicate) and P2954 (calcium borax), were tested.

Table 1: Empirical formulas for some of the glazes used in the present experiments.

| Glaze | CaO* | MgO* | $K_2O$* | $Na_2O$* | $Fe_2O*_3$ | $Al_2O_3$ | $SiO_2$ | $B_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| A1 | 0,441 | 0,343 | 0,120 | 0,076 | 0,019 | 0,285 | 2,574 | 0,412 |
| A11 | 0,735 | - | 0,139 | 0,123 | 0,003 | 0,377 | 3,709 | - |
| C5.2 | 0,283 | 0,524 | 0,110 | 0,058 | 0,025 | 0,219 | 2,498 | - |
| C5.7 | 0,422 | 0,409 | 0,089 | 0,078 | 0,002 | 0,244 | 3,761 | - |
| C5.9 | 0,421 | 0,408 | 0,090 | 0,078 | 0,002 | 0,281 | 3,664 | - |
| C8.1 | 0,252 | 0,539 | 0,121 | 0,060 | 0,029 | 0,226 | 2,051 | - |
| C8.2 | 0,233 | 0,570 | 0,116 | 0,048 | 0,034 | 0,203 | 1,866 | - |
| C8.3 | 0,181 | 0,597 | 0,132 | 0,049 | 0,041 | 0,219 | 1,992 | - |
| C14 | 0,374 | 0,354 | 0,143 | 0126 | 0,003 | 0,403 | 5,018 | - |
| C14.1 | 0,370 | 0,349 | 0,147 | 0,131 | 0,003 | 0,381 | 4,982 | - |
| C14.2 | 0,319 | 0,290 | 0,205 | 0,183 | 0,004 | 0,521 | 6,499 | - |
| B11.1 | 0,794 | - | 0,108 | 0,095 | 0,002 | 0,300 | 3,054 | - |

*RO group

In Table 1 is given the empirical formula of the compositions of the glazes, which were used in testing the different amounts of MgO and CaO in comparison to the amounts of $Al_2O_3$ and $SiO_2$.

**The thickness of glazes.** From the glazes several test samples were prepared by which the suitable thickness of the glazes was tested. In addition the reactions of two similar layers were tested by samples in which figures were drawn with the same glaze as was used as a thick glaze layer on the clay body. The tile samples were covered with a glaze of extra thickness. The technique for applying the figure was tested with the glazes A1 and A11. On the glazed test objects streaks were drawn with another glaze in order to see how they reacted together.

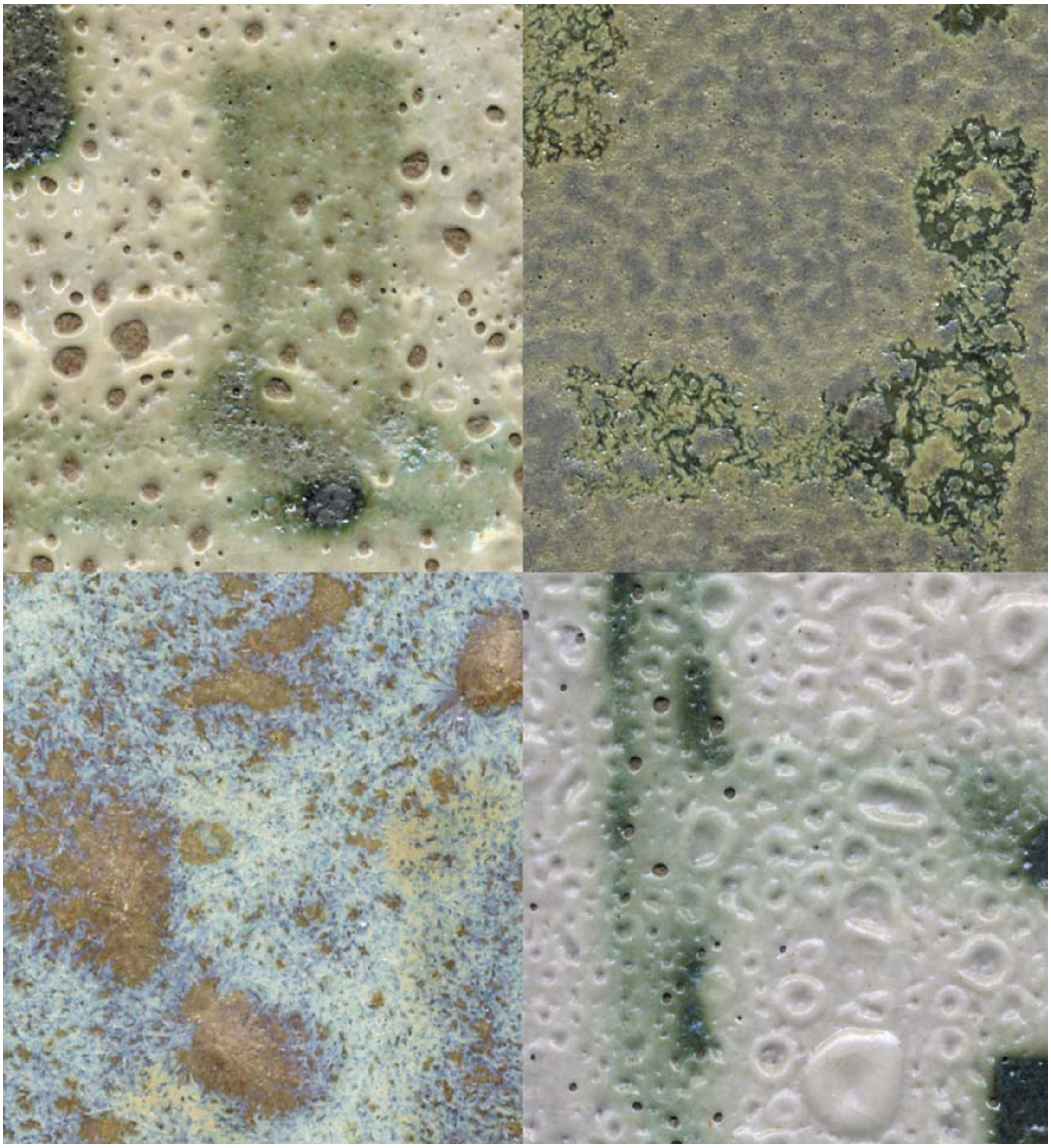

Fig: Different surfaces of test glazes.

**Colouring of the tested glazes**. A few well melted but opaque mixtures of glazes ware coloured and tested as black “temmoku”-glazes. To the glazes four metal oxides were added: 4w-% CuO, 6w-% $Fe_2O_3$, 2w-% CoO and 1w-% $Cr_2O_3$. Some of the glazes melted as a brown to black surface. The “temmoku”-glazes formed a covering and thick layer on the clay body.

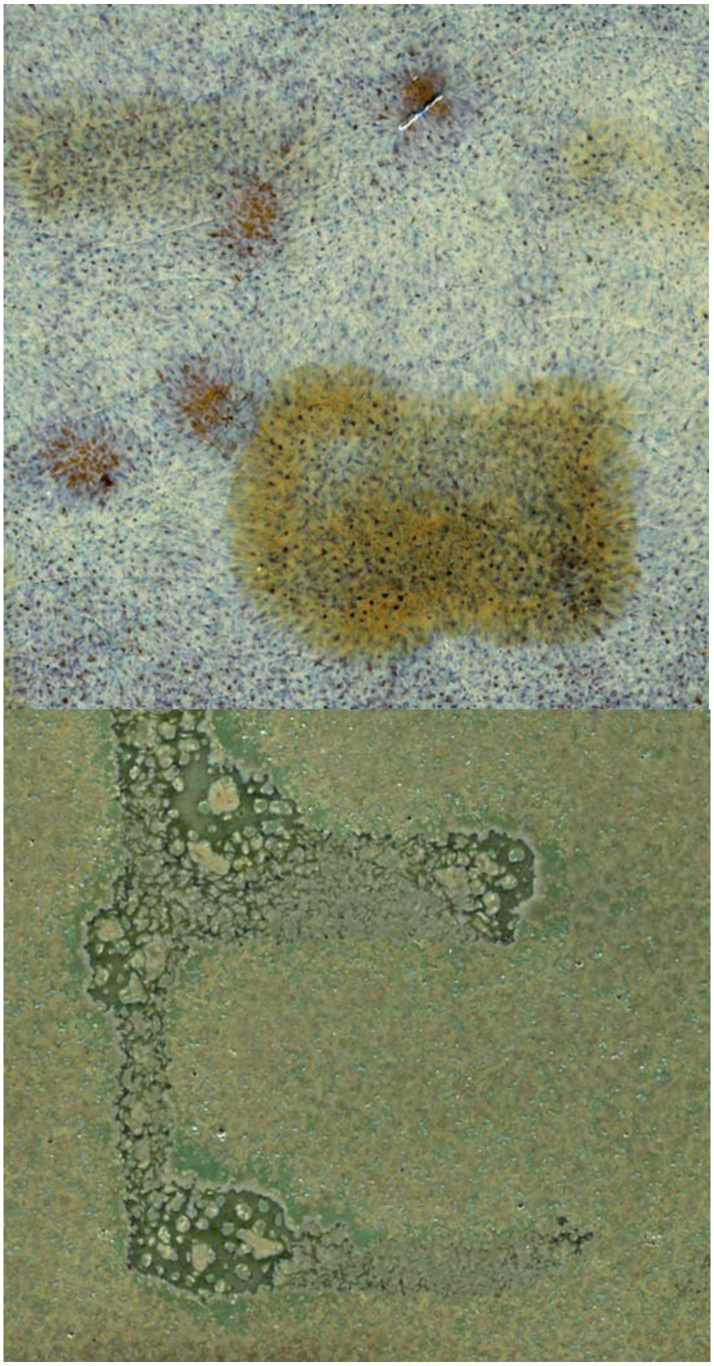

Fig: The glazes react with the clay body of Soap Stone. The iron oxide gives the bluish colour and chromite gives green colour.

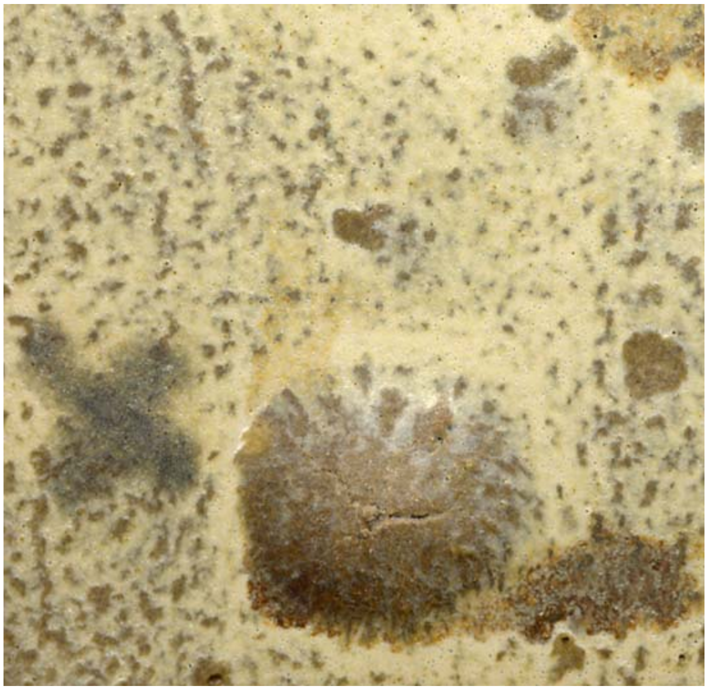

Fig: An opaque and rough glaze surface on the clay body of Soap Stone

## Results

The amount of soapstone has a great impact on which glaze should be selected. The borax frit (P2953) tested in the sample A1 was not a suitable glaze raw material in the present cordierite clay body. The use of phlogopite mica as a glaze raw material worked well, giving opaque surface layers and lightly beige colours after firing. Magnesium oxide caused opaque and poor melting properties, however, by decreasing the amount of magnesium oxide a more transparent and glossy glaze is obtained. At high temperatures MgO is an effective frit, which increases the temperature stability of the glaze and hinders cracking. Together with calcium oxide MgO reacts at the surface of the claybody and fastens the glaze to the clay body. It also increases the mechanical stability of the glaze. Also a high content of calcium oxide helps in the formation of the glaze on the clay body.

**Glaze surfaces**. The glaze A1 melts and forms a glossy glaze on the cordierite clay body. When comparing the ratios of the melting oxides in the glaze A1 it is seen that the amount of MgO is less and the amount of CaO is higher than for the other glazes in the mixture of the glazes. The composition of glaze A1 includes the frit P2953, and the glaze reacts with the surface of the cordierite clay body because of the boron oxides. The clay body sucks the glaze layer into itself. In the glaze A11 there occur no MgO but the content of CaO is high. There is a high amount of $SiO_2$ in the glaze C5.9, which forms a glasslike surface layer. According to the testing of the materials and their empirical formula the oxides in the glazes 14, 14.1 and 14.2 give good surface properties. In the same glazes relatively high amounts of $Al_2O_3$ and $SiO_2$ can be observed in comparison with other tested glazes.

Table 2: The properties of the fired glazes.

| Properties | A1 | A11 | C5.2 | C5.7 | C5.9 | C8.1 | C8.2 | C8.3 | C14 | C14.1 | C14.2 | B11. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Glossy | ●● | ●●● | ●● | ●● | ●●● | ●● | ●● | ●●● | ●●● | ●● | ●● | ●● |
| Matt | - | - | ● | ●● | ●● | ● | ● | ●● | ● | ● | ● | - |
| None melt | - | ● | ● | - | - | - | - | - | - | - | - | - |
| Melted | ●● | ●●● | ● | ●● | ●●● | ●●● | ●●● | ●●● | ●●● | ●●● | ●●● | ●● |
| Opaque | - | - | ●● | ● | ● | ● | ● | ● | ●●● | ●●● | ●●● | ●●● |
| Transparent | - | ●●● | - | - | - | - | - | - | - | - | - | - |
| Rough | ● | - | ● | - | - | - | - | - | - | ● | - | ● |
| Smooth | ● | ●●● | ● | - | - | ●●● | ●●● | ●●● | ●●● | ●● | ●● | ● |

Marks: Good = ●●●, Reasonable = ●●, Poor =●, None result = -

Quartz and boron oxide form two phases, which cannot be mixed with each other, when they form the glass in glazes [2]. This is seen as spots and irregular surfaces. The clay body causes difficulties for the glaze to melt. The layer of the glaze is thin and stays at the surface of the clay body.

The glaze sample C5.2 was separately tested at a higher firing temperature of 1240 °C. The glaze C5.2 then melts more rapidly but is also boiling more forming an interesting and smooth surface structure. The thin layer of the same glaze is also soaked into the clay body. Magnesium oxide affects the colour of iron oxide and together with calcium oxide the colour becomes yellowish. When the glazes are thick they contain wholes but at the same time they are smooth and glossy.

The glazes C5.7 and C5.9 are lightly cream coloured and covers well. Painted iron oxide on the glaze is yellow brown. When testing the surfaces of glazes the layers should be extra thick. A lot of the glazes have holes on their surface but they are smooth and only slightly glossy. They can because as surfaces on for example construction elements. Especially the glaze C8.3 has a good glaze layer when burned at 1220°C, but it boils. It soaks into the surface of the clay body if the temperature is further increased. It can be generally concluded that the glazes C8.1 C8.3 form a glaze surface in all cases. The ratio between aluminium oxide and quartz respect to magnesium oxide are in accordance with the firing temperature. These glazes also form a silicate surface for the clay body containing soapstone.

## Conclusion

From the empirical formula is seen that alum oxide and quartz have the eutectic ratio both with magnesium oxide and calcium oxide alone and together so that the silicate formed is suitable for a clay body containing soapstone. The adjustment of the temperature is important for the formation of the surface. The glazes which are suitable to be used with clay bodies containing soapstone work within a limited temperature range [2]. For some glazes a temperature increase of 20°C caused boiling or at a decrease in temperature of 20°C no melting of the glaze occurred. The surfaces of the glazes are exceptionally cracking on the clay bodies containing soapstone, which is due to the increase of alkalis within the RO-group. When the content of magnesium oxide is increased in relation to changes of aluminium oxide and quartz the surface of the glaze on the clay body containing soapstone is intact. Magnesium oxide glues the glaze to the clay body. The thickness of the glaze layer is of importance for its stability. The increase or decrease of magnesium oxide changes the viscosity of the glaze and decreases the cracking. The properties of phlogopite mica as a raw material for cordierite clay bodies are very suitable. However, in a larger scale the knowledge about its suitability in manufacturing of ceramic glazes is poorly known. The use of minerals from the mining industry is an ecological decision.

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