

DETERMINATION OF MOLASSE SANDSTONE VARIETIES AND THEIR PROPERTIES AT THE MINSTER OF SALEM (FRG) WITH SPECIAL REGARDS TO GEOCHEMISTRY

BESTIMMUNG DER AM MÜNSTER ZU SALEM VERBAUTEN MOLASSESANDSTEINE UND IHRER EIGENSCHAFTEN UNTER BESONDERER BERÜCKSICHTIGUNG GEOCHEMISCHER ASPEKTE

DÉTERMINATION DES GRÉS MOLASSE UTILISÉS POUR LA CATHÉDRALE DE SALEM ET DE LEURS PROPRIÉTÉS EN TENANT COMPTE DES ASPECTS GÉOCHIMIQUES

(This paper is a preliminary summary of a report which will be issued in the beginning of 1994)

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SUMMARY

Molasse sandstones - wide spread building stones in the subalpin region of South Germany - can have a similar macroscopic appearance, but a quite different petrographic composition and - in consequence - a quite different petrophysical behaviour. The aim of this report is to evaluate the number of molasse sandstone varieties and their properties at the Minster of Salem to support restoration workers in developing a suitable concept for stone conservation. Beyond microscopic methods and the determination of parameters like porosity, water uptake etc. geochemical characterization with means of x-ray fluorescence analysis (XRF) is presented.

ZUSAMMENFASSUNG

Molassesandsteine - verbreitete Naturbausteine im süddeutschen Voralpengebiet - sind sich bezüglich ihres makroskopischen Erscheinungsbildes sehr ähnlich, können aber eine ganz unterschiedliche petrographische Zusammensetzung aufweisen und sich bezüglich ihrer gesteinsphysikalischen Eigenschaften stark voneinander unterscheiden. Ziel der vorliegenden Untersuchungen ist es, die Anzahl der am Münster zu Salem verbauten Molassesandsteinvarietäten aus dem Bodenseeraum festzustellen und ihre Eigenschaften einzugrenzen, um damit dem Restaurator das notwendige

Rüstzeug für ein geeignetes Konservierungskonzept in die Hand zu geben. Neben den üblichen Methoden der Mikroskopie und der Bestimmung von Parametern wie Porosität, Wasseraufnahme etc. wird die geochemische Charakterisierung mittels der Röntgenfluoreszenzanalyse (RFA) behandelt.

RÉSUMÉ

Les grés molasse - pierres de construction naturelles très répandues en bordure des régions des Alpes en Allemagne du Sud - se ressemblent en vue de leur aspect macroscopique, mais peuvent avoir une composition pétrographique très différent. Il est le but de ce rapport d'évaluer le nombre des différents grés molasse et leurs qualités pour soutenir les restaurateurs à l'établissement d'une conception appropriée de conservation des pierres. En plus des méthodes microscopiques et la détermination de paramètres comme porosité, absorption de l'eau etc. la caractérisation géochimique par analyse-fluorescence aux rayons-X est présentée.

Keywords

molasse sandstone, Minster at Salem, x-ray fluorescence analysis, geochemistry of molasse sandstone, petrophysical properties of molasse sandstone, investigation methods

1. INTRODUCTION

The name "molasse sandstone" refers to all sandstones, which were formed by debris flow (especially from the west part of the Swiss Alps) into the northern "molasse basin" due to the mountain building process of the Alps during the tertiary age. Special layers of this 4000 m thick embankment were used as building stones since the Middle Ages in the southern part of Baden-Württemberg and Bavaria. The Minster of Salem/Lake Constance belongs to the historic monuments, which are built of molasse sandstone. Because of its geological origin as a million of years lasting debris flow from the Alps, the composition and properties of the different types of molasse sandstone are quite different - even in narrow stratigraphic neighborhood [1]. Till now there was neither a systematical survey regarding the different varieties of molasse sandstone from the Minster of Salem nor any investigation of differences in

their properties. This basic knowledge however is necessary to develop a suitable concept of stone conservation for the partly heavy damaged facades at the Minster in Salem.

Another reason for this work is to support our interpretation of nondestructive thermographic and moisture measurements, which were/are performed at this building (see in this journal FRICK & WEISS: "Thermographic Behaviour of the North Facade of the Minster in Salem").

2. SCHEME OF INVESTIGATION

Before starting with the explanations it is necessary to give a definition of "variety" within this paper: it means a sandstone which shows similar mineralogical composition and petrophysical properties.

In figure 1 the way to evaluate the different varieties is shown. In a first step it was necessary to gain enough material from the building without overlooking a potential variety. The selection of different types of molasse sandstone at Salem Minster is not trivial, because every variety has almost the same macroscopic appearance (see table 1): fine grain sizes, green-blue to green-yellow to green-brown colours, a changing content of mica flakes and glauconite grains, carbonatic cementation, with exception of orientated micas no other special characteristics of bedding.

Therefore not only the criterion of appearance but also the build in age was of interest. The latter was dated by Mr. Knapp - an art historian with a special knowledge about the Minster of Salem. In the beginning of this way we thought of about 7 to 10 potential molasse sandstone varieties, which are shown in table 1. Most samples (final sum: 17) originated from material, which was removed in former restauration phases and stored on the loft inside the minster. Only in one case it was necessary to drill a borehole into the wall of the building to gain a special variety.

In a second step we decided to make a first differentiation with means of simple and not very time intensive methods as: water uptake under special conditions, determination of bulk and solid density, evaluation of total

Scheme of investigation

Step 1

Sampling of "molasse sandstone" varieties at the Minster of Salem; selection of individual stones due to their macroscopic appearance and their age of build in to the historic building

Step 2

Determination of simple parameter at every sample

- ① water absorption under special conditions (DIN 52103)
- ② bulk density
- ③ solid density
- ④ total porosity
- ⑤ hygroscopic absorption of water from the air
- ⑥ total amount of carbonate

Step 3

Preliminary variety classification, selection of samples for further investigations

Step 4

Complementary determination of mineralogical and petrophysical properties

/fabric/petrography/geochemistry	/petrophysical properties
<ul style="list-style-type: none"> ① study of composition and fabric on thin sections using polarizing microscope ② phase analysis with x-ray diffraction - especially for the investigation of composition of clay minerals ③ study of structure with scanning electron microscopy ④ x-ray fluorescence analysis for the determination of major, minor and trace elements 	<ul style="list-style-type: none"> ① measurement of the coefficient of water absorption and penetration ② determination of pore size distribution by means of mercury porosimetry ③ evaluation of isothermal swelling ④ measurement of thermic expansion ⑤ determination of ultrasonic velocity as a characteristic for grain bond and modulus of elasticity

Step 5

Final classification of molasse sandstone varieties at the Minster of Salem

Figure 1: scheme of investigation

Table 1: Potential molasse sandstone varieties at the Minster in Salem on the basis of build in age and macroscopic appearance

Sample	Build in age	Variety	Part of building	Macroscopic appearance
SAL 1	ca. 1300	1	"Obergraden" buttress no. IX	grey-green, fine grain sizes, glauconite- and mica bearing, iron stainings, calcitic
SAL 9	ca. 1300	1	nave	green, fine grain sizes, glauconite-bearing, with mica, iron stainings, calcitic
SAL 12	ca. 1300	1	inner molding	green, fine grain sizes, glauconite-bearing, calcitic
SAL 2	ca. 1300	2	"Obergraden" buttress no. IX	yellow-green, fine grain sizes, much mica, glauconite-bearing, calcitic
SAL 3	ca. 1300	2	"Obergraden" buttress no. IX	yellow-green, fine grain sizes, mica, glauconite-bearing, iron stainings, calcitic
SAL 15	ca. 1300	2	"Obergraden" - choir	yellow-green, fine grain sizes, mica- and glauconite-bearing, calcitic
SAL 16	ca. 1300	2	"Obergraden" - choir	yellow-green, fine grain sizes, mica- and glauconite-bearing, iron stainings, calcitic
SAL 17	ca. 1300	3	inner eastern wall of choir	yellow-green, fine grain sizes, mica- and glauconite-bearing, iron stainings, calcitic
SAL 4	ca. 1300	4	"Obergraden" buttress no. IX	yellow-green, fine grain sizes, much mica, glauconite bearing, calcitic
SAL 13	ca. 1300	4	"Obergraden"	green-yellow, fine grain sizes, mica- and glauconite-bearing, calcitic
SAL 8	ca. 1420	5	probably "Obergraden"	green-yellow, fine grain sizes, mica- and glauconite-bearing, calcitic
SAL 5	ca. 1470/90	6	buttress no. VI	green, fine grain sizes, glauconite-bearing, calcitic
SAL 6	1883/91	7	western facade	green, fine grain sizes, glauconite-bearing, iron stainings, calcitic
SAL 7	18. Jh	evtl. 8	western facade	green, fine grain sizes, glauconite-bearing, calcitic
SAL 10	18. Jh.	evtl. 8		yellow-green, fine grain sizes, glauconite-bearing, iron stainings, calcitic
SAL 11	18. Jh	evtl. 9		yellow-green, fine grain sizes, glauconite-bearing, iron stainings, calcitic
SAL 14	15. Jh. (?)	evtl. 10	buttress no. XII	yellow-green, fine grain sizes, mica- and glauconite-bearing, iron stainings, calcitic

porosity, gasometric measurement of total carbonate content, isothermal hygroscopic absorption of water at a relative a humidity of 76 and 100 %. Chapter 3 gives a short description of methods and measured properties. Two reference samples of unweathered "Rorschacher molasse sandstone" (a present building stone in the Lake Constance area) were integrated into all tests.

After realization of above mentioned procedures it was possible to make a preliminary group classification in a third step and therefore to reduce the number of samples (with exception for x-ray fluorescence analysis) for further investigations.

In step 4 more costly examinations (listing see figure 1) were done with the reduced sample set, to get additional informations about the mineralogical and petrophysical properties of the investigated samples. Especially the observation of composition and fabric in thin sections with means of polarizing microscope allow to understand the measured petrophysical stone properties and to reach the final aim of this work: a classification of the molasse sandstone varieties used at the Minster in Salem.

3. METHODS

3.1. Water uptake

Water uptake was measured according to DIN 52103 with evaluation of the parameters

W_{a_a} : water uptake under atmospheric pressure [wt.-%]

W_{a_v} : water absorption under vacuum and under 150 bar [wt.-%]

S: coefficient of water saturation [] ($S = W_{a_a}/W_{a_v}$)

To measure the hygroscopic water uptake all samples were stored in covered vessels with saturated salt solution of NaCl (76 % relative humidity) respectively pure water (100 % relative humidity) to the equilibrium between air moisture and stone moisture. The amount of water absorption in relation to dry sample mass describes two parameters:

- $W_{(76\%)}$: hygroscopic water uptake at 76 % r.h. [wt.-%]
 $W_{(100\%)}$: hygroscopic water uptake at 100 % r.h. [wt.-%]

With the knowledge of maximum water uptake W_{a_v} it is possible to calculate the degree of pore filling as a consequence of hygroscopic water absorption.

To measure capillary properties of the molasse sandstone varieties experiments similar to DIN 52617 were carried out. Four parameters were investigated:

- w : water absorption coefficient [$\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1/2}$]
 B : water penetration coefficient [$\text{mm}/\text{s}^{1/2}$]
 W_{a_k} : water capacity [vol.-%]
 S_t : saturation coefficient as result of capillary absorption []

For a detailed description of all methods mentioned above with recommendations of specific literature see [2].

3.2. Porosity and density

To determine total porosity, bulk and solid density there exists a simple method [2]: one totally saturates a porous sample under vacuum and/or pressure with water and determines three weights: first that of the dry sample, second that of the completely watersaturated sample and third that of the same sample in water with buoyancy. With these three weights it is possible to calculate

- Θ_s : solid density [g/cm^3]
 Θ_b : bulk density [g/cm^3]
 n : total open porosity [vol.-%]

While the bulk density depends on both - mineral composition and pore volume of the sample, the solid density is only correlated with mineralogical properties. It was the idea, that the solid density therefore would be a sensible parameter for differentiating stone varieties.

3.3. Mercury porosimetry

A second chance to get an independent value of total porosity is by mercury porosimetry. The main advantage of this method however is the possibility of a quantitative measurement of pore radii distribution. For details of the penetration of mercury in relation of pressure into pore spaces of a porous body see [3]. These investigations were done by means of a "Carlo Erba Strumentazione" mercury porosimeter up to a pressure of 2000 bar.

3.4. Ultrasonic velocity

The determination of ultrasonic velocities of stones is an excellent procedure to gain some information about grain bond. The shorter the propagation time through the sample the better the grain bond and in most cases one may empirically assume a higher elasticity and a higher density of the rock. The experiments were carried out with a Nicolet oscilloscope.

3.5. Gasometric determination of carbonate content

If acid (e.g. HCl) contacts carbonate (e.g. CaCO₃) the following chemical reaction takes place:



In a closed system - like the "SCHEIBLER-apparatus" - one is able to measure the volume of the CO₂-gas and therefore to calculate the total mass of carbonate reacting with acid (detailed description of the "SCHEIBLER-method" in [4]). Dolomite CaMg(CO₃)₂ reacts slower than calcite CaCO₃ with hydrochloric acid - so there is the chance to separate the different carbonatic phases of a rock powder by observing the dynamic of the process of gas development.

3.6. X-ray diffraction analysis

To identify mineral phases of the different molasse sandstone varieties, the method of x-ray diffraction analysis was used in two ways: at first we investigated powder specimens to get a survey of the complete mineral composition and secondly we prepared and measured some orientated clay mineral samples to determine the clay minerals (in a first step of preparation the clayey part of the sandstone has to be separated from the rest).

3.7. Polarizing microscopy

Thin sections give a very useful information especially about fabric (e.g. visible porosity, grain bond and sizes etc.) and mineral composition of rocks. To get quantitative information about petrography and pore space the point counter method with a minimum of 500 points per section was used. We distinguished the following components:

- rock fragments (rf)
- quartz (qz)
- feldspars (fsp)
- mica (mi)
- heavy minerals (hm)
- cement (cm)

To get a better characterization of rock fragments, these were divided into their calcitic part, their dolomitic part and into a rest containing cherts, mica schists, slates, tuffs and other silicate rocks. The cements were subdivided into carbonate, clay, silicate and iron (e.g. iron oxides and -hydroxides) cements. The classification of sandstones was done according to FÜCHTBAUER [5].

3.8. X-ray fluorescence analysis

3.8.1. Basic principles

A detailed description of the method of x-ray fluorescence analysis may be found in [6], [7] and [8]. Very simplified we have the following principle: samples prepared as powder pellets or fused glass discs are excited with x-ray radiation (the x-ray tube operates with a high voltage between 10 and 100 kV). Interaction of this primary radiation with atoms of the sample causes ionization of discrete orbital electrons. During the subsequent electronic rearrangement (excited electrons fall back to ground state) a characteristic secondary fluorescent radiation due to the excited element is emitted. This emission is measured by a suitable x-ray spectrometer. The concentration of an element in a sample and the emitted fluorescent radiation are normally linearly correlated. With a set of standards with well known chemical composition one is able to measure these intensity-concentration relationships for a lot of elements. For unknown samples one has to measure for every element of interest the characteristic intensity and to calculate its concentration with means of standard samples calibration lines. Theoretically all elements with an ordinal number $Z > 5$ can be measured by this method.

Beyond the reliability of the measurement device or sample preparation the accuracy of every intensity-concentration line depends on

- matrix effects
- spectral line overlap interferences.

Matrix effect means absorption-enhancement effects caused by the influence of all other elements in the sample. For example there is a chance of absorption of K_{α} radiation from element A by element B which emits a K_{α} radiation by itself with another wave length because of this secondary excitation. As a result of this effect the measured intensity of element A will be too low, that of element B will be too high. There are two ways to minimize matrix effects. First is to investigate only standards and unknown sample with almost the same chemical composition (= matrix) - because in this case the matrix effect

is for every sample the same and therefore neglectible. The second way is to use suitable mathematical correction procedures, which is for practical reasons more common than the first way. These practical reasons are:

- in geologic practice normally one has to investigate rocks with a wide geochemical spectrum
- the number of available natural geostandards (certificated rocks, minerals and soils) is limited.

For correcting spectral overlap interferences (e.g. V K_{α} with Ti K_{β}) there is also a suitable mathematical correction procedure necessary.

3.8.2 Measurement device

Our spectrometer is a SRS 300 Siemens Spectrometer with an Rh-tube, which is operated by Spectra AT Software V. 2.1 (developed by Socabim/Paris). To minimize matrix effects we use SFP 1 software (Socabim/Paris), which calculates for every interesting element theoretical α -values (= characteristic parameters for intensity correcture) according to the "fundamental parameter model" and in relation to the chemical composition of the sample. It is also possible to correct spectral overlap interferences by a mathematical procedure within this software.

At present all samples (standards and unknowns) are prepared as fused glass discs; the rock powder to flux ratio is 1:5, whereas the rock powder is ignited before disc preparation. The flux consists of $Li_2B_4O_7$.

At present 10 major and minor (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) and 13 trace elements (Nb, Zr, Y, Sr, Rb, Ga, Zn, Cu, Co, Ni, Cr, V and Ba) can be measured.

4. RESULTS

4.1. Preliminary molasse sandstone classification by means of simple investigation methods

By aid of the measurement of the hygroscopic water uptake there was no possibility for differentiation of the investigated molasse sandstones. Storing all samples at an relative humidity of 76 % caused a gain in weight of 0.4 to 0.6 wt.-%, in case of a humidity of 100 % the hygroscopic water absorption increased to 0.6 to 1.0 wt.-%.

We obtained better results with measuring water uptake under different pressure regimes - under atmospheric pressure and under 150 bar. In both cases two groups with different absorption behaviour could be separated. Group A absorbed 2.7 to 5.0 wt.-% water without and 3.2 to 7.0 wt.-% under pressure. Group B demonstrated a higher water uptake: 7.0 to 11.0 without and 10.0 to 14.5 wt.-% under pressure. The saturation coefficient S showed no definite results. Within group A it varied between 0.66 and 0.92 whereas in group B this value was more constant with about 0.70 to 0.75.

Porosity measurements confirmed the assumption of at least two different groups of stones. Group A has a porosity of 8.5 to 16.5 vol.-%, which increases in group B to 21.5 to 31.5 vol.-%. The same demonstrated the evaluation of bulk density, which amounts to 2.28 to 2.54 g/cm³ in case of group A and 1.88 to 2.13 g/cm³ in case of group B.

A first hint to the existence of more than two molasse sandstone groups or varieties gave the investigation of solid density. The spectrum reached from 2.70 to 2.75 g/cm³ (pure quartz: 2.65 g/cm³), whereas group A and group B were separated at a density value of 2.72 g/cm³. Because of significant deviations in every group more than two types of stone became probably.

The determination of calcitic respectively dolomitic carbonate content supported the assumption of more than two varieties. Dolomite content ranged normally in an intervall of 2 - 4 wt.-%, but in case of sample SAL 17 it increased on about 15 wt.-%. Most samples of group A regularly have a

calcite content of about 20 wt.-%, but we found samples with 33 and 46 wt.-%. In group B 17 to 33 wt.-% calcite were measured.

The investigation of total amount of carbonate and solid density demonstrated that there are more than two different molasse sandstone varieties built into the Minster at Salem. To detect these other varieties - which were up to now included in group A or B - it was necessary to use some other methods.

4.2. Additional investigation methods for final classification of molasse sandstone varieties at the Minster of Salem

Most of the investigation methods ("Step 4") listed in figure 1 are finished meanwhile, some other work still have to be continued, e.g. study of structure of different varieties with scanning electron microscopy, clay mineral determination with x-ray diffraction analysis or evaluation of hygric swelling and thermal expansion.

Because of the results described in 4.1. we were able to select representative samples for group A and B and other samples, we are not quite sure how to class, for further investigations.

By means of x-ray diffraction analysis the assumption of SAL 17 being an own variety was confirmed. Because of the height of dolomite peaks in x-ray diffraction pattern the special position of this stone was clearly apparent. Even though the x-ray diffraction diagram of group A and B distinctly differ - all three varieties are composed of an identical mineral spectrum (quartz, alkali feldspars, calcite, dolomite, mica or illite, clay minerals), only the contents diverge from each other. With present knowledge and x-ray diffraction analysis three varieties and their mineral phases could be characterized and named.

The names for the varieties were established because of their macroscopic appearance. Samples, which belong to the "blue variety" often show blueish colours; for the samples of the "yellow variety" brown-yellow stainings

because of oxidized iron are very common and sample SAL 17 representing the "brown variety" demonstrates a typical brown colour in the wet state. But the given names do not mean that there is a possibility to classify the different molasse sandstones only because of their colours!

The mineral composition and the relative mineral contents respectively the relative height of the peaks in the x-ray diffraction pattern are:

Group A ("Blue variety"): quartz high, alkali feldspars high, calcite medium, dolomite low, mica low

Group B ("Yellow variety"): quartz medium, alkali feldspars medium, calcite medium, dolomite low, mica medium

Group C ("Brown variety"): quartz medium, alkali feldspars low, calcite high, dolomite high, mica low

These three varieties are even clearly visible in thin sections under the microscope. To class sample SAL 9 into group A, B or C was problematically, because this sample shows another fabric than respectively petrographic composition similar group A. Therefore a fourth group D ("Green variety" because of green colour of SAL 9) had to be introduced. Under the microscope the main characteristics of group A, B, C and D are (see also figures 2 a-d):

Group A: (blue v.) Quartz, feldspars and rock fragments are bond together by a calcitic and clayey cement, which fills almost the whole intergranular space, so under the light microscope pores nearly are not visible . Heavy minerals or mica are rare, calcite only exists in form of sparitic cement but not in form of lithoclasts. With a very high probability all samples included in the blue variety belong to the "Rorschacher molasse sandstone". The rock forming processes for this type of stone describes [9].

Group B: (yellow v.) Silicate rock fragments are the main component, feldspar and quartz contents are lower than in group A. The cement consists of sparitic calcite and clay, but calcite can be found as lithoclasts too. The calcitic lithoclasts often are heavily recrystallized, so that the primary fabric is not visible any

more. Mica and heavy minerals are more common than in group A. Because of the absence of a high content of calcite cements, the fabric demonstrates a network of large pore channels, which have a very perfect connection with each other.

Group C: (brown v.) The main component of this variety are rock fragments, whereas dolomitic and calcitic lithoclasts are very common. The latter consist of micritic limestones or they show similar recrystallization fabrics like in group B. The components often are bond together by a silicate cement (e.g. quartz overgrowth), but total percentage of cement is very low. Calcite seldom appears as cement, mica or heavy minerals are found only sometimes. The pore system is very similar to group B.

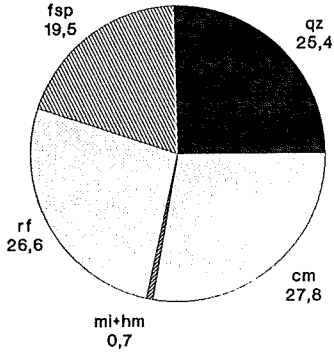
Group D: (green v.) Main characteristic of this variety is a very high content of cement - which normally consists of sparitic calcite. In spite of the high calcitic cement content a clearly visible open porosity still exists, but the connection between the pore spaces is poorer than in case of group B or C.

The usefulness of geochemical investigation by means of x-ray fluorescence analysis will be discussed in 4.3.. Because of limited space in this journal the results of measurements of petrophysical properties of different varieties must be extremely short.

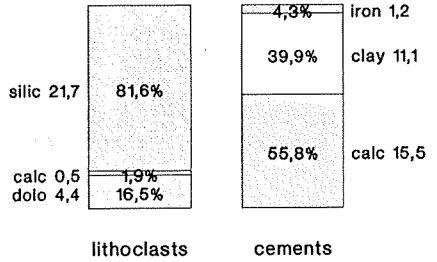
Evaluation of water absorption coefficient w respectively water penetration coefficient B demonstrates very great differences between blue (group A) and yellow (group B) variety. Measurements of w and B for the first type of stone result in values of $w < 1.5 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1/2}$ and of $B < 0.30 \text{ mm}\cdot\text{s}^{-1/2}$; the second type of stone displays values of $4 < w < 30 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1/2}$ and $0.8 < B < 3.5 \text{ mm}\cdot\text{s}^{-1/2}$. This means, that w or B between blue and yellow variety may differ with an order of magnitude.

The difference between these two varieties can be characterized with means of ultrasonic velocity as well as with mercury porosimetry. The velocity for the blue variety is $> 2500 \text{ m/s}$, for yellow variety normally $< 2200 \text{ m/s}$; with ultrasonic velocities and bulk densities it is possible to calculate or - because limited of the not very suitable geometry of the investigated samples - to

Petrographic composition
"Blue variety"(group A)



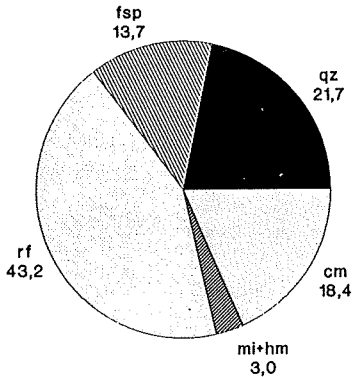
relative and absolute contents
of lithoclasts and cements



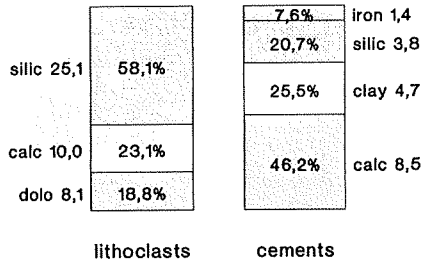
dolo = dolomite
silic = silicate
calc = calcite

Figure 2a: Petrography of the blue variety

Petrographic composition
"Yellow variety"(group B)



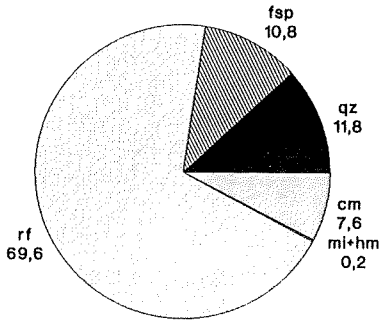
relative and absolute contents
of lithoclasts and cements



dolo = dolomite
silic = silicate
calc = calcite

Figure 2b: Petrography of the yellow variety

Petrographic composition
"Brown variety"(group C)



relative and absolute contents
of lithoclasts and cements

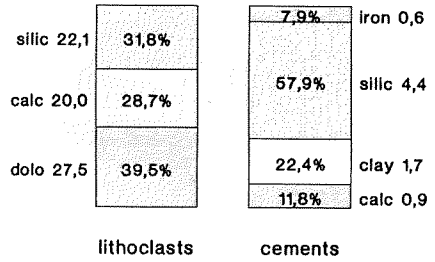
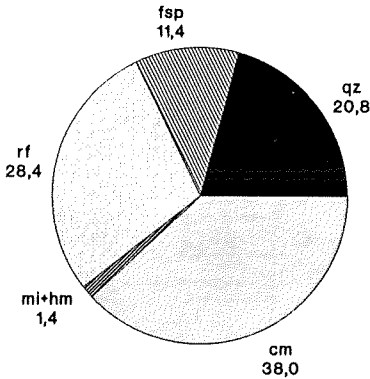


Figure 2c: Petrography of the brown variety

dolo = dolomite
silic = silicate
calc = calcite

Petrographic composition
"Green variety"(group D)



relative and absolute contents
of lithoclasts and cements

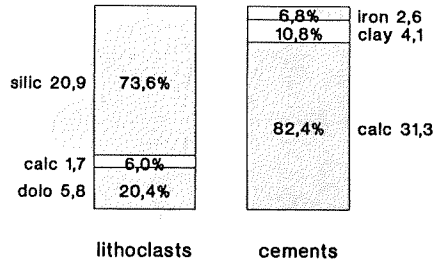


Figure 2d: Petrography of the green variety

dolo = dolomite
silic = silicate
calc = calcite

estimate dynamic modulus of elasticity: for the yellow variety it is $< 5 \text{ kN/mm}^2$, for the blue variety $15 - 30 \text{ kN/mm}^2$.

In spite of the fact that the yellow variety has the greater total pore volume, the blue variety has a greater absolute pore volume in the dimension of micropores ($\phi < 0.1 \mu\text{m}$). The average pore size diameter is for both varieties situated in the intervall $0.1 \mu\text{m} < \phi < 7.5 \mu\text{m}$, but it is distinctly smaller for the blue than for the yellow type of stone. In pore classes $> 7.5 \mu\text{m}$ one find only an absolute pore volume of maximum 1 vol.-% for group A, but up to 10 vol.-% for group B. The petrophysical properties of the brown variety (group C) differ - as result of a similar pore system - only slightly from the yellow one. Because of the small size of sample SAL 9 representing group D (green variety), we could not measure all properties for this stone type.

4.3. Geochemical investigations with XRF for variety classification

The results of the measurement of major, minor and trace elements are listed in table 2 (major and minor elements) respectively in table 3 (trace elements). Table 4 demonstrates the correlation coefficients between every measured element; with this calculation method it is easier to understand the relations between elements - a necessary step for our future work: understanding chemical processes in molasse sandstone weathering.

Looking at table 4 there are a lot of correlations between elements - positive and negative -, which would be all worth to be explained here. But let me feature a few examples to demonstrate the usefulness of geochemical investigations for the determination of molasse sandstone varieties.

One way to distinguish different varieties is to characterize their major element composition. Figure 3 shows a ternary diagram where the three edges of the triangle represent SiO_2 (quartz and most silicate rock fragments), the sum of CaO , MgO and LOI (carbonates) and the sum of Al_2O_3 , Na_2O and K_2O (alkali feldspars and clay minerals). To represent every sample in this diagram one has to project the values listed in table 2 of the above mentioned components to a sum of 100 wt.-% (with only indirect regards to the oxides

Table 2: Geochemical composition of the investigated molasse sandstone varieties - major and minor elements

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Sum
	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]
Blue Variety												
SAL6	64,77	0,21	7,25	1,92	0,05	2,48	9,85	1,57	1,96	0,24	9,88	100,17
SAL5	63,34	0,26	7,09	2,81	0,05	2,86	10,12	1,40	1,68	0,16	10,49	100,26
RM1	62,34	0,26	7,41	1,99	0,05	2,79	10,53	1,60	1,84	0,24	10,83	99,90
SAL7	61,68	0,28	6,88	1,87	0,06	2,53	11,33	1,45	1,78	0,23	11,30	99,39
RM2	61,66	0,21	7,50	2,02	0,05	2,64	11,03	1,69	1,87	0,21	11,13	100,02
SAL12	60,55	0,29	7,06	2,79	0,06	3,13	11,39	1,29	1,64	0,19	11,87	100,24
SAL10	60,45	0,19	6,87	1,66	0,07	1,91	13,31	1,52	1,82	0,20	12,32	100,31
Yellow variety												
SAL8	59,51	0,36	7,51	2,46	0,05	3,04	11,66	1,42	1,79	0,25	12,08	100,14
SAL14	56,79	0,34	7,29	2,23	0,06	2,79	13,46	1,29	1,74	0,23	13,43	99,64
SAL11	55,19	0,33	6,94	2,06	0,07	3,11	13,59	1,44	1,54	0,29	14,03	98,59
SAL4	55,08	0,36	7,06	2,18	0,07	2,93	14,74	1,36	1,69	0,23	14,41	100,11
SAL16	52,81	0,32	6,79	2,05	0,08	2,78	16,47	1,29	1,60	0,22	15,71	100,13
SAL2	52,37	0,36	6,81	2,13	0,08	2,86	16,43	1,25	1,61	0,23	15,67	99,80
SAL13	52,23	0,38	6,78	2,27	0,07	3,06	16,57	1,31	1,52	0,27	15,81	100,27
SAL3	48,30	0,31	6,20	1,87	0,12	2,51	19,71	1,17	1,43	0,20	17,90	99,74
SAL15	47,91	0,28	5,97	1,81	0,10	2,43	20,55	1,12	1,42	0,20	18,45	100,24
SAL1	47,25	0,29	6,18	1,83	0,08	2,50	19,28	1,22	1,44	0,19	19,73	99,99
Green variety												
SAL9	39,37	0,19	4,72	1,52	0,09	2,19	26,09	1,36	1,20	0,15	22,79	99,66
Brown variety												
SAL17	35,03	0,11	2,93	0,91	0,03	7,48	24,78	0,73	0,72	0,03	27,69	100,44

LOI: Loss of ignition
Total iron as Fe₂O₃

Table 3: Geochemical composition of the investigated molasse sandstone varieties - trace elements

Sample	Nb [ppm]	Zr [ppm]	Y [ppm]	Sr [ppm]	Rb [ppm]	Ga [ppm]	Zn [ppm]	Cu [ppm]	Co [ppm]	Ni [ppm]	Cr [ppm]	V [ppm]	Ba [ppm]
<i>Blue Variety</i>													
SAL6	3	62	30	212	71	5	30	12	6	17	43	30	222
SAL5	1	75	23	234	64	6	34	12	4	23	51	36	182
RM1	3	116	29	222	69	7	39	5	4	32	56	34	216
SAL7	3	77	28	242	68	7	30	1	3	17	57	31	230
RM2	1	69	24	237	71	9	35	10	4	21	53	31	223
SAL12	3	72	27	253	63	5	36	5	3	21	62	35	194
SAL10	1	74	21	229	65	6	26	10	3	21	48	25	203
<i>Yellow variety</i>													
SAL8	5	147	34	265	68	8	36	4	4	21	81	44	224
SAL14	4	179	30	285	68	6	38	5	7	23	72	40	211
SAL11	4	109	31	262	60	5	35	7	5	23	72	37	190
SAL4	4	230	31	290	62	6	35	10	3	27	80	35	190
SAL16	3	171	29	314	61	6	34	14	4	28	73	31	194
SAL2	3	240	30	318	60	4	32	18	7	23	81	35	199
SAL13	7	200	30	326	56	5	36	6	3	22	79	32	196
SAL3	1	173	26	356	53	6	30	12	1	24	68	28	206
SAL15	1	137	25	366	53	3	28	10	4	20	57	32	165
SAL1	2	153	28	349	56	6	32	14	1	26	68	29	184
<i>Green variety</i>													
SAL9	1	69	20	402	44	2	24	12	3	17	50	18	142
<i>Brown variety</i>													
SAL17	1	31	13	400	27	2	15	13	3	12	29	16	85

Table 4: Correlation matrix for 24 elements for molasse sandstones on basis of "Salem" sample set

	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	LOI	Nb	Zr	Y	Sr	Rb	Ga	Zn	Cu	Co	Ni	Cr	V	Ba	
SiO2	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
TiO2	0.23	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Al2O3	0.89	0.58	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe2O3	0.66	0.63	0.76	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MnO	-0.39	0.35	-0.07	-0.09	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MgO	-0.50	-0.38	-0.68	-0.43	-0.48	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CaO	-0.98	-0.25	-0.87	-0.67	0.50	0.36	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Na2O	0.80	0.11	0.79	0.42	-0.16	-0.70	-0.73	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K2O	0.94	0.35	0.95	0.60	-0.17	-0.70	-0.89	0.87	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P2O5	0.61	0.74	0.84	0.53	0.18	-0.67	-0.58	0.66	0.74	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
LOI	-0.99	-0.32	-0.93	-0.71	0.30	0.57	0.96	-0.82	-0.96	-0.68	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nb	0.26	0.67	0.41	0.41	-0.21	0.01	-0.34	0.16	0.27	0.64	-0.30	1	-	-	-	-	-	-	-	-	-	-	-	-	-
Zr	-0.07	0.85	0.31	0.29	0.51	-0.26	0.07	-0.10	0.13	0.50	-0.01	0.45	1	-	-	-	-	-	-	-	-	-	-	-	-
Y	0.51	0.86	0.77	0.62	0.11	-0.50	-0.53	0.43	0.64	0.89	-0.58	0.72	0.63	1	-	-	-	-	-	-	-	-	-	-	-
Sr	-0.97	-0.07	-0.80	-0.53	0.53	0.36	0.97	-0.79	-0.87	-0.52	0.94	-0.23	0.22	-0.39	1	-	-	-	-	-	-	-	-	-	-
Rb	0.93	0.40	0.97	0.65	-0.19	-0.67	-0.90	0.85	0.99	0.75	-0.96	0.31	0.15	0.68	-0.86	1	-	-	-	-	-	-	-	-	-
Ga	0.72	0.29	0.76	0.49	-0.24	-0.36	-0.74	0.67	0.75	0.50	-0.71	0.23	0.13	0.48	-0.68	0.78	1	-	-	-	-	-	-	-	-
Zn	0.66	0.73	0.87	0.82	-0.01	-0.53	-0.68	0.58	0.71	0.77	-0.72	0.57	0.47	0.81	-0.55	0.77	0.68	1	-	-	-	-	-	-	-
Cu	-0.43	-0.20	-0.35	-0.29	0.31	0.11	0.45	-0.33	-0.34	-0.38	0.43	-0.48	0.18	-0.30	0.42	-0.38	-0.31	-0.39	1	-	-	-	-	-	-
Co	0.32	0.16	0.32	0.22	-0.28	-0.04	-0.34	0.21	0.35	0.27	-0.34	0.24	0.15	0.31	-0.31	0.35	0.03	0.23	0.08	1	-	-	-	-	-
Ni	0.32	0.57	0.57	0.44	0.28	-0.45	-0.31	0.34	0.43	0.52	-0.37	0.20	0.58	0.55	-0.25	0.46	0.50	0.73	0.04	-0.05	1	-	-	-	-
Cr	0.13	0.97	0.52	0.54	0.40	-0.38	-0.15	0.11	0.29	0.70	-0.22	0.61	0.98	0.81	0.01	0.34	0.31	0.68	-0.10	0.12	0.58	1	-	-	-
V	0.67	0.75	0.82	0.81	-0.14	-0.36	-0.71	0.41	0.67	0.72	-0.71	0.58	0.44	0.82	-0.56	0.73	0.58	0.85	-0.42	0.45	0.48	0.66	1	-	-
Ba	0.83	0.50	0.92	0.57	0.02	-0.71	-0.79	0.78	0.93	0.82	-0.87	0.36	0.26	0.73	-0.73	0.94	0.77	0.74	-0.40	0.23	0.45	0.45	0.67	1	-

Values demonstrating a high chance of positive or negative correlation ($r > 0.85$) between two elements are marked.

TiO₂, Fe₂O₃, MnO and P₂O₅). It may be recognized that the different molasse sandstone varieties can be characterized by this method. The inverse proportionality between the SiO₂-content and the total amount of the components CaO, MgO and LOI, representing the carbonatic components of the different types of stone, is obviously. Also table 4 displays very high negative correlation coefficients between SiO₂ on the one and CaO, LOI and Sr on the other side. But there are still some insecurities, especially in differentiating the blue from the yellow variety.

Figure 4 demonstrates an improved chance to separate the last two varieties by means of selected major elements. This diagram shows the SiO₂ content as a function of the sum of Al₂O₃, Na₂O and K₂O for every sample. It is clearly visible that the blue variety has simultaneously the highest SiO₂- respectively $\Sigma(\text{Al}_2\text{O}_3\text{-K}_2\text{O-Na}_2\text{O})$ -contents. The high correlation coefficients between Na₂O/K₂O, Na₂O/Al₂O₃, K₂O/Al₂O₃, Na₂O/SiO₂ and K₂O/SiO₂ show (see table 4), that most of the Na- and K-ions are built into alkalifeldspars and clay minerals (e.g. glauconite, smectite). This assertion is confirmed by microscopic investigations, which demonstrate the highest alkalifeldspar fraction and the highest clay mineral content for the blue variety (see figures 2a-d).

The different varieties can also be distinguished by some of the trace elements, for example Sr. Almost all Sr-ions are built into the lattice of calcite (see $r(\text{CaO/Sr})$ in table 4) - a high Sr-value automatically means a high content of calcite. Because of this fact, the Sr-values of the yellow variety are normally higher than for the blue one (figure 5).

One of the best possibilities to distinguish the different types of molasse sandstone varieties is to regard the elements belonging to the heavy mineral association. Every heavy mineral association in a sandstone is controlled by the geology of the erosion area and by the sedimentation process. Therefore a great chance exists, that different molasse sandstones sedimentated at different times and in different areas, have another heavy mineral association.

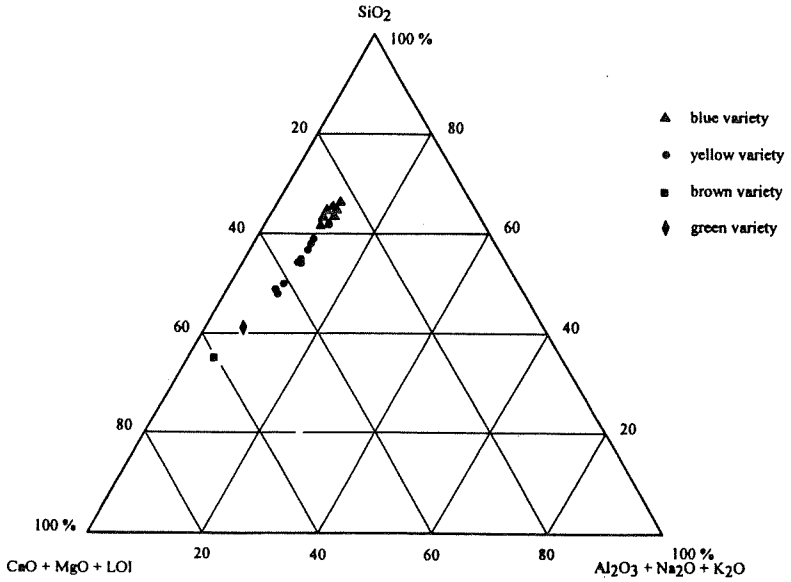


Figure 3: Diagram SiO₂ - (Al₂O₃ + Na₂O + K₂O) - (CaO + MgO + LOI)

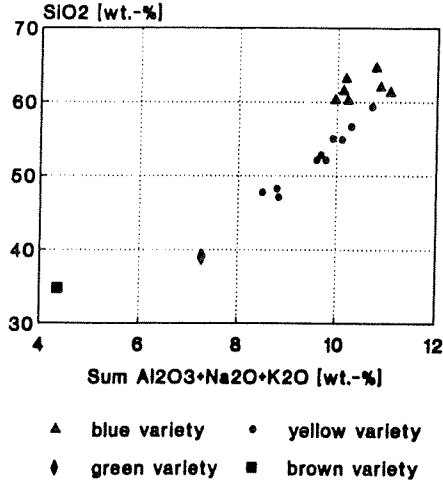


Figure 4: Diagram SiO₂ - (Al₂O₃ + Na₂O + K₂O)

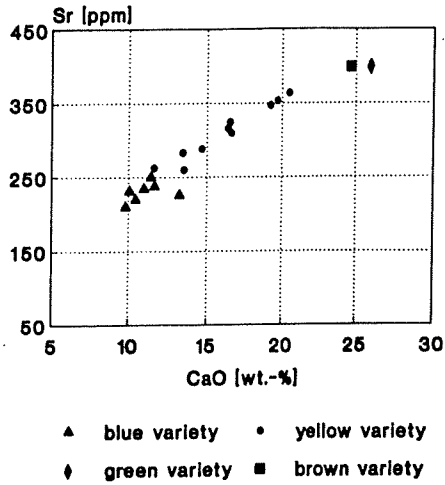


Figure 5: Diagram CaO - Sr

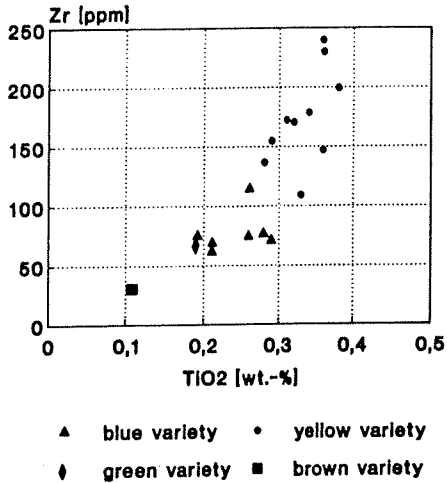


Figure 6: Diagram TiO₂ - Zr

In case of the Salem sample set the elements Ti, Zr, Cr, P and Y are positively correlated. The Ti-content of the samples is controlled by the amount of Ti-bearing heavy minerals like rutile (TiO_2), anatase (TiO_2) or titanite ($\text{CaTi}[\text{SiO}_4](\text{O},\text{OH},\text{F})$). Zr occurs in zircon $\text{Zr}[\text{SiO}_4]$, Cr is an important component of basaltic spinels (e.g. chromite: FeCr_2O_4) and the rare earth element Y can be found in xenotime, a yttrium phosphate (YPO_4). Most of P is part of apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$), a very common heavy mineral in sandstones. Figure 6 shows the relation of the Zr-content as function of TiO_2 -content for every sample. It is apparent, that the yellow variety always dispose of higher TiO_2 - and Zr-values than the other three molasse sandstone groups. The microscopic observations confirm the geochemical analyses: from yellow to blue/green to brown variety a decreasing content of heavy minerals can be observed.

Geochemical measurements and petrographic investigations show the correctness of the assumption, that the determination of elements occurring in heavy minerals is an indicator for separating different molasse sandstone varieties.

5. CONCLUSIONS

Simple investigation methods are not sufficient enough to distinguish the real number of molasse sandstone varieties build into the Minster of Salem. When using additional methods like x-ray fluorescence analysis it is possible to solve this problem, because every variety has a characteristic composition of major, minor and trace elements. At present state of knowledge we are able to separate four different molasse sandstone varieties at this building. The classification of the different types of molasse sandstones is essential for a stone conservation concept. The investigation of the petrophysical properties has shown, that there are significant differences between the varieties. Because of the simultaneous determination of geochemical, petrophysical and mineralogical properties, we now are able to predict the characteristics of a further sample with only determining one of the mentioned properties. This can facilitate continuing investigations at this building.

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