Private Sector Development Programme South Caucasus

Country Component Georgia

Fundamental ceramic investigations of 3 clay quarries to prepare Qvevri Pots

Tbilisi, July 2016

german cooperation
DEUTSCHE ZUSAMMENARBEIT

Implemented by:
giz Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH

german cooperation
DEUTSCHE ZUSAMMENARBEIT

Implemented by: giz Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH

DasKeramikinstitut

Content

1. First remark

The KI Keramik Institut GmbH (named following **KI**) expressed great respect to the producers of Qvevris in Georgia, who produce clay Qvevris since thousands of years by hand. Such clay articles are very complicated to manufacture, especially account to their big size and the situation of the raw materials (clays), what is giving in Georgia.

It is a unique ceramic performance!

Nevertheless we have to make sure in these days and age, to maintain the knowledge of the production of these big Qvevris on the base of a millennia long experience on the one side but in combination with the newest ceramic perceptions.

2. Current situation and task

Pots produced from burning clay are a major element of Qvevri wine production and it´s a part of your identity.

The raw materials for these pots are taken from three major and two minor sites in the clay quarries.

The shaping of the raw material are carried on by specialized pot manufacturers and the firing process bases on traditional procedure.

It´s in the nature of clay, that the chemical-physical composition change from one site to the other and even within varies. It is necessary to make systematical research of the properties of each quarry to transform this knowledge into a ceramic reproducible production process with properties of the Qvevris as desired.

2. Current situation and task

The first step is done to determine the basic ceramic properties of three clay quarries

- No – I, 1…10: Vill. **Vardisubani**, Telavi, Georgia
- No – II, 1….10: Vill. **Tkemlovana**, Chiatura, Georgia
- No – III, 1…10: Vill. **Satsable**, Zestoponi, Georgia.

3. Overview about all investigations

- **chemical composition** and the **grain size distribution** for all samples of each quarry (10 per quarry) was the basic for all further analyses

- next step: 3 samples of each ten per quarry was selected single samples with the lowest, middle and highest Al2O3-content (lowest, middle and highest clay content) to see the complete range of property regarding to the **mineralogical composition** and the **fire behavior**

3. Overview about all investigations

- **Preparations** and measurements **for the samples of each quarry** in the labs of KI unfired/ fired) → **<u>strength, water absorption</u>**
- In addition the samples of **<u>unfired and fired bodies from the Georgian producers</u>** were also analyzed in the same way
- **<u>Summary: the research gives all main characteristics in case of technological properties</u>**

4. Applied analyses and measurements

Determination of mineralogical and chemical composition

- Measurement of crystalline phases by XRD (x-ray diffraction)
- preparation of 3 single parts to determine all hard components like quartz, feldspar (and other, which could be disturb the ceramic mind) as well as clay minerals inclusive swellable and non swellable of them and the existing iron compounds
- Measurement of elements Fluorine … Uranium by XRF (X-ray fluorescence analysis) melted beats
- Measurement at dried pressed tablets for determining Fluorine, Sulphur and Chlorine

4. Applied analyses and measurements

Determination of mineralogical and chemical composition

- Determination of LOI (loss of ignition) at 1000°C (mass difference before and after thermal treatment)
- Measurement of organic, inorganic and total carbon by carbon analyzer
- Measurement of water soluble salts by ICP in an eluate

DasKeramikinstitut

4. Applied analyses and measurements

Why were these parameters analyzed?

- All properties of the Qvevris (generally of every clay product) at first depend on mineralogical and chemical composition of the used raw clays.
- All mineral phases, the hard components and the plastic components (clay minerals) have a certain function in a ceramic body - during shaping and firing
- With this knowledge it is possible to capture workability, especially plasticity of the clays in a quarry and the required firing temperature.

4. Applied analyses and measurements

- Chemical results: Each of the analyzed oxides has one or more functions in a ceramic body in shaping as well as firing.

- Sulfur is an indicator for existing water soluble salts
- Chlorine is very aggressive against stainless steel
- Fluorine is not good with respect to environment and food safety

- Carbon compounds:
- Organic carbon → black core inside the fired body
- Inorganic carbon → less density and less stability of the fired body

- Water soluble salts are the minerals transferring from the clay to the Qvevri wine

5. Determination of grain size distribution

- measurement of grain size distribution was accomplished in two parts

1. the percentage >63µm was carry out by manual wet sieving with 5 different mash sizes, the sieve residues on each sieve were weighted and listed into a table

2. the measurement <63µm was measured by SediGraph until 0,5µm in small steps

All dates were completed together in one table per sample and then per quarry

5. Determination of grain size distribution

Why it was analyzed?

- Determination of grain size distribution is the second basic analyses to get an idea for workability of a clay raw material
- Clay minerals are very fine particles below 10 µm. While the grain size of the hard material components, show in majority larger gran size.
- Because only clay particles are responsible for plasticity they are the basic of shaping. The detailed values of grain size distribution show the suitability of a raw material to produce clay vessels like Qvevris.

5. Determination of thermal behavior by dilatometer (expansion curves)

- for this thermal analyses samples 25x5x5 mm^3 were shaped and grinded
- after drying, measurement in a dilatometer
- in result expansion- and shrinkage values as a function of certain firing temperature are obtained

5. Determination of thermal behavior by dilatometer (expansion curves)

Why it was accomplished?

- Different mineral phases inside raw clays in connection with a certain fineness lead to a different expansion and shrinkage during firing. These values are not possible to calculate and must be measured.
- Expansion-/ shrinkage measurements by dilatometer give a comprehensive overview to all parts of samples during firing → at which temperatures expansion of a sample and at which temperature the sintering process begins.

5. Determination of water absorption

- producing of samples by hand shaping in gypsum moulds/ vacuum extrusions
- drying and firing in an electrical kiln at 1000°C
- determination of water absorption by cooking for 2 hours and cooling in room temperature 4 hours
- calculating of the water absorption values by weighing before and after treatment

- Why it was accomplished?
- water absorption of a fired clay product like the Qvevris express the impermeability of the clay vessels
- the lower the water absorption values, the more dense the Qvevris are
- he higher the density of the Qvevris, the higher the strength is
- water absorption isn’t possible to calculate and has to measure

6. Discussion of results
6.1 Vardisubani

- Mineralogical analyzes [table 1a…c]

- Relatively high content of hard materials quartz and feldspar (46…50%)
- Feldspar: mix of different kind of feldspar, the percentage of potassium feldspar is significant more higher
- quartz + potassium feldspar are high melting components

- percentage of clay minerals in sum 45…49%
- 2- and 3-layer clays: only 32…34%; more 3 layer clay minerals, swellable and non swellable (only 5% kaolinit as the main 2-layer clay mineral)

DasKeramikinstitut

6. Discussion of results

6.1 Vardisubani

Protocol of Analysis: Pr. I/2

Company:	Keramik-Institut; Ossietzkystr. 37a; D-01662 Meißen
Phone:	+49 3521-463-510 or 515
Our Sample-No.	X044/16/02
Method:	X-Ray-Diffractometry (XRD)/ triple preparation
Customer:	GIZ Georgia *KI 231/16g*
Arrival:	06.04.2016

Mineral Phase	mean value[1] weight%	Max-Min[2] weight%
Below all phases of standard mineral analysis are listed and all phases found by qualitative mineral phase analysis.		
Σ Orthoclase/Plagioclase K-Feldspar + mix crystal line, Na- to Ca-Feldspar	11	1
Quartz	37	2
Σ Three-sheet minerals **Sum, for details look table below	28	3
Σ Two-sheet minerals Kaolinite+Halloysite+Fireclay	5	3
Σ Four-sheet minerals Chlorite + Chamosite ("Fe-Chlorit")	13	2
Hematite α-Fe_2O_3	< 2	1
Calcite $CaCO_3$	< 2	1
Σ Dolomite / Ankerite $CaCO_3 \times MgCO_3 + CaCO_3 \times FeCO_3$	< 2	1
Augite	3	1
Σ Anatase / Rutil[3] TiO_2	1	1
Goethite α-FeOOH	< 2	1
Residue analytical mistakes, TOC	2	1

**Three-sheet minerals		
Smectite -/ Montmorillonite-Group[4]	9	3
Mixed Layer Illite/Smectite[4]	< 5	3
Illite (Hydromuscovite)[6]	< 5	3
Muscovite (Mica's, Sericite)	19	3
Corrensite[4,5]	< 5	3

[1] e.g. "< 2" value below LLD of e.g. 2 weight%

[2] difference between Max- u. Min-value of analysis on 3 samples

[3] TiO_2-value from chemical analysis

[4] swellable clay-minerals, [5] swellable Chlorite

[6] estimated from separately determined LOI/TOC and grain size distribution (if available)

Dr.-Ing. Jens Petzold

6.1 Vardisubani

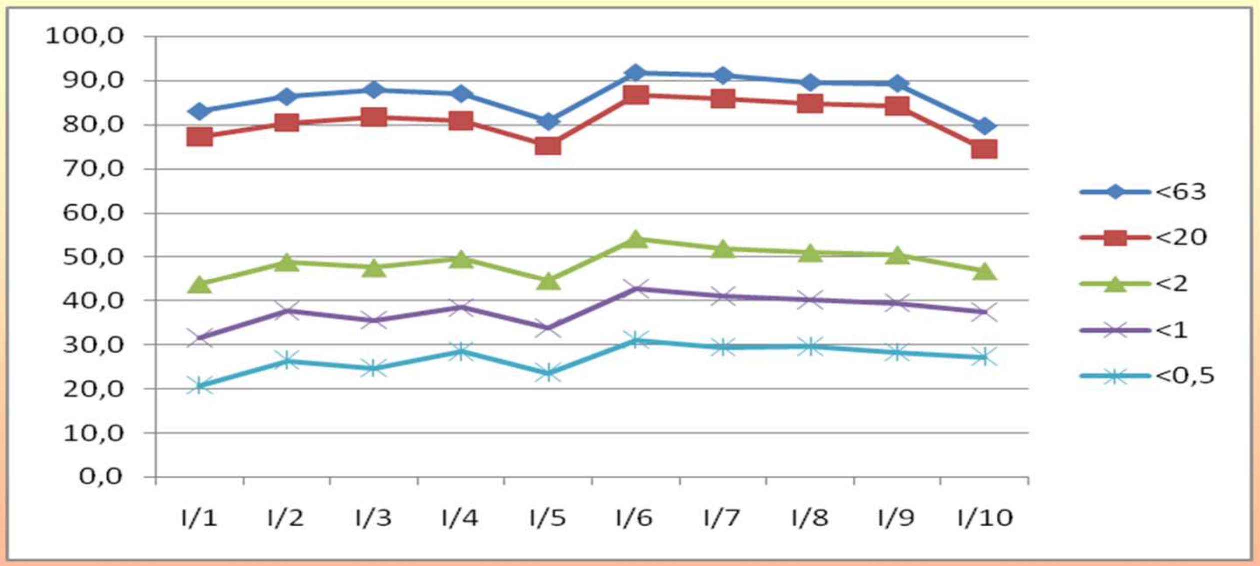
- In 2 cases → inorganic carbon was analyzed. (a really small influence on firing between 700…900°C).

- Note: In Vardisubani fired body still exists a small amount of loss of ignition due to organic carbon in the fired body. That means, firing of Vardisubani was not ready.

6.1 Vardisubani

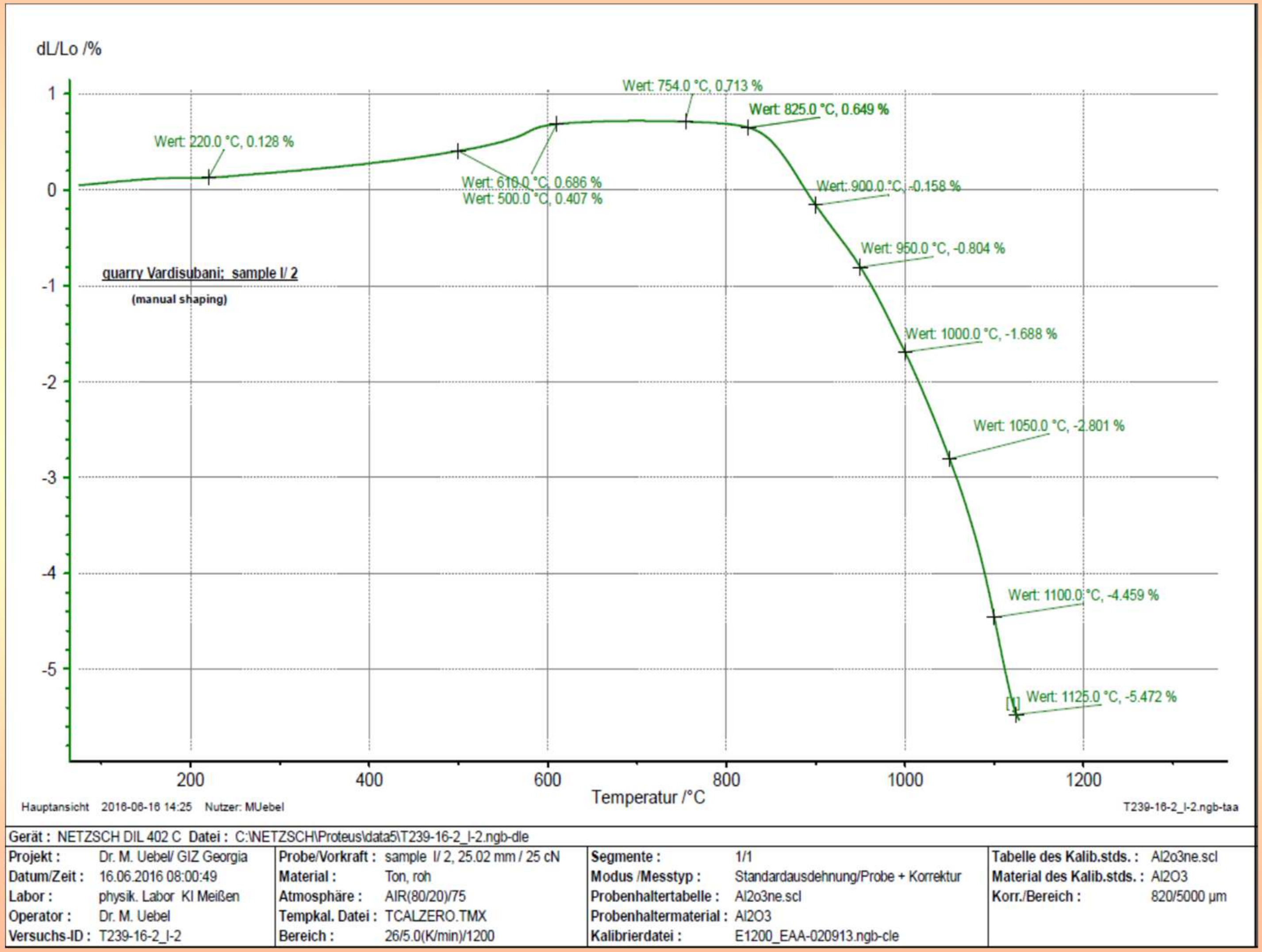
Vill. Vardisubani, Telavi
sampling by Karaulashvili Tamazi

	I/1	I/2	I/3	I/4	I/5	I/6	I/7	I/8	I/9	I/10	Std_var
<63	83,0	86,3	87,9	87,0	80,7	91,7	91,1	89,5	89,3	79,7	4,2
<20	**77,3**	**80,5**	**81,7**	**80,9**	**75,2**	**86,8**	**85,9**	**84,8**	**84,3**	**74,5**	4,4
<2	**43,7**	**48,8**	**47,5**	**49,5**	**44,5**	**54,1**	**51,9**	**50,9**	**50,4**	**46,7**	3,3
<1	31,6	37,7	35,6	38,4	33,9	42,7	41,0	40,2	39,5	37,4	3,4
<0,5	20,8	26,5	24,7	28,5	23,7	31,1	29,4	29,6	28,3	27,3	3,1



6.1 Vardisubani Thermal behavior

.



DasKeramikinstitut

6.1 Vardisubani

In result is to state:

- **The jump in the graph of quartz transformation is very high, connected with tensions inside the samples!**
- The beginning of sintering was measured at about 815…825°C (begin of decreasing length of samples) and goes on continuously until the end of measurements at 1100°C…1150°C.
- measured firing shrinkage values at 1100°C: 3,80…5,27%!
- So the dilatometrical measurements reflect the different mineralogical and chemical composition and the high differences in grain size distribution too.

6.1 Vardisubani

dilatometrical firing shrinkage [%]

	Sample I/ 1	Sample I/ 2	Sample I/ 6	Vardisubani
1000°C	-1,47	-1,69	-1,85	-1,19
1050°C	-2,36	-2,80	-3,09	-1,98
1100°C	-3,81	-4,46	-5,27	-3,70
1125°C		-5,47	(> 6)	
1150°C	-5,81			

6.1 Vardisubani

- Temperature controlled drying was realized in steps over some days in an air circulation dryer:
- 24h in lab at room temperature, covered with silk paper
- 24h at 30°C
- 24h at 40°C
- 24h at 60°C
- 24h at 110°C

- The average value of **dry shrinkage for samples Vardisubani is → 7,1%** (very high value and is closed connected with danger of so called dry cracks)
- The average value of **dry bending strength for samples Vardisubani is → 10,0 MPa** (value is very high for a clay body and allows a good handling without danger of demolition.

6.1 Vardisubani

The following table shows the results for the Vardisubani samples in comparison. Number I/ 1 – 2 and -6 prepared in the KI.

‘Vardisubani’ is the fired body, which was sent to the Institute.

All measured dates are seen in [table 8].

	water absorption [%]	open Porosity [%]	bulk density [g/cm^3]
sample I/ 1	10,13	20,96	2,069
sample I/ 2	7,90	15,79	2,118
sample I/ 6	6,93	14,82	2,138
Vardisubani (orig)	14,35		

6.1 Vardisubani

- Relatively high values of water absorption mean that the fired bodies of all samples from Vardisubani are not dense in result of firing process.
- Contrariwise there is a high open porosity. So in this state it is necessary to accomplish a surface finish to realize a blocking pore for a dense Qvevri.
- The comparison between the sample from a Qvevri Vardisubani and the samples from Ceramic Institute shows a significant difference in the firing result. It reflects the very high influence of the technology of shaping, the firing conditions on the result of the fired Qvevris as well as the strong variation inside the quarry Vardisubani!

6.1 Vardisubani

- measurement of → acid solution of the fired body from Vardisubani
- This test was accomplished by imitation of a regular test by using a chemical acid.
- The test was carried out by using the original Georgian wine. It was the aim to prove the wine solvable amount of the Vardisubani Qvevri in fired state.
- **wine soluble percentage of a fired Qvevri Vardisubani → 0,08 mass % 40g per 1000 litre**

DasKeramikinstitut

6.1 Vardisubani

- **wine soluble percentage of a fired Qvevri Vardisubani → 0,08 mass %   40g per 1000 litre**

Protocol of Analysis: VAR, burned

Our Sample-No. 219/04/16   KT: 231/16G

Method: XRF-Analysis according to DIN 12677

Customer: GIZ Georgia

Arrival: 4/6/2016

Sampling: by costumer, date unknown

Chemical analysis of dried sample

	mean val.	standard deviation
	weight%	weight%
SiO2	67,09	0.2
Al2O3	15,92	0.2
Fe2O3	7,29	0.02
TiO2	0,81	0.02
CaO	1,90	0.02
MgO	2,06	0.02
K2O	2,53	0.02
Na2O	1,05	0.02
BaO	0,10	0.02
ZrO2	0,02	0.02
HfO2	<0.02	0.02
SrO	<0.02	0.02
ZnO	<0.02	0.02
MnO2	0,27	0.02
Cr2O3	0,03	0.02
V2O5	0,02	0.02
P2O5	0,15	0.02
LOI 1000 °C	0,71	0,02

ff1_schmAl

6.2 Tkemlovana

Mineralogical analyses [9a..c]

- relatively high content of hard materials quartz and feldspar (non-plastic components vary from 38…49%).

- On the side of feldspar a mix of different kind of feldspars, the percentage of potassium feldspar is significant more higher

- percentage of clay minerals total : 46…52%
- two- and three layer clay minerals: 32…34%.
- 4-layer clay minerals: 8…9%.

- ratio of 2- to 3-layer clay minerals different to Vardisubani
- 14…25% 2-layer clay minerals (Kaolinite) and 22…27% 3-layer clay minerals, under it 11…17% swellable one

DasKeramikinstitut

6.2 Tkemlovana Mineralogical analyses

Protocol of Analysis: Pr. II; 6

Company:	Keramik-Institut; Ossietzkystr. 37a; D-01662 Meißen
Phone:	+49 3521-463-510 or 515
Our Sample-No.	X044/16/05
Method:	X-Ray-Diffractometry (XRD)/ triple preparation
Customer:	GIZ Georgia *KI 231/16g*
Arrival:	06.04.2016

Mineral Phase	mean value[1] weight%	Max-Min[2] weight%
Below all phases of standard mineral analysis are listed and all phases found by qualitative mineral phase analysis.		
Σ Orthoclase/Plagioclase K-Feldspar + mix crystal line, Na- to Ca-Feldspar	10	1
Quartz	32	2
Σ Three-sheet minerals **Sum, for details look table below	27	3
Σ Two-sheet minerals Kaolinite+Halloysite+Fireclay	16	3
Σ Four-sheet minerals Chlorite + Chamosite ("Fe-Chlorit")	9	2
Hematite α-Fe_2O_3	< 2	1
Calcite $CaCO_3$	< 2	1
Σ Dolomite / Ankerite $CaCO_3 \times MgCO_3$ + $CaCO_3 \times FeCO_3$	< 2	1
Σ Anatase / Rutil[3] TiO_2	1	1
Goethite α-FeOOH	4	1

**Three-sheet minerals		
Smectite -/ Montmorillonite-Group[4]	17	3
Mixed Layer Illite/Smectite[4]	< 5	3
Illite (Hydromuscovite)[6]	< 5	3
Muscovite (Mica's, Sericite)	10	3
Corrensite[4,5]	< 5	3

[1] e.g. "< 2" value below LLD of e.g. 2 weight%
[2] difference between Max- u. Min-value of analysis on 3 samples
[3] TiO_2-value from chemical analysis
[4] swellable clay-minerals, [5] swellable Chlorite
[6] estimated from separately determined LOI/TOC and grain size distribution (if available)

6.2 Tkemlovana

The chemical analyses

- For quarry Tkemlovana no inorganic carbon was analyzed.
- See [table 12].

- In opposite to Vardisubani in the fired body a very small LOI was found. That means, in this case firing was nearly complete regarding to outgoing organics. Here is seen the advantage of low carbon contents of raw materials!

6.2 Tkemlovana

The chemical analyses

Grain size distribution

- Tkemlovana: exorbitant wide range of grain size distribution.
- result of the variation of clay minerals on the one side and hard components on the other side
- So for quarry Tkemlovana the statement is still more given that the workability is very different from one to another position in the quarry.

- Absolutely the most of the values at 20µm as well as at 2µm are too low (for instance in comparison of a brick plastic mass as a good criterion for the question: what is a sufficient plasticity and which values at 20µm/ 2µm should be). So in case of Tkemlovana plasticity of the clay is hindered. Influences to firing in general are discussed in connection with thermal behavior.

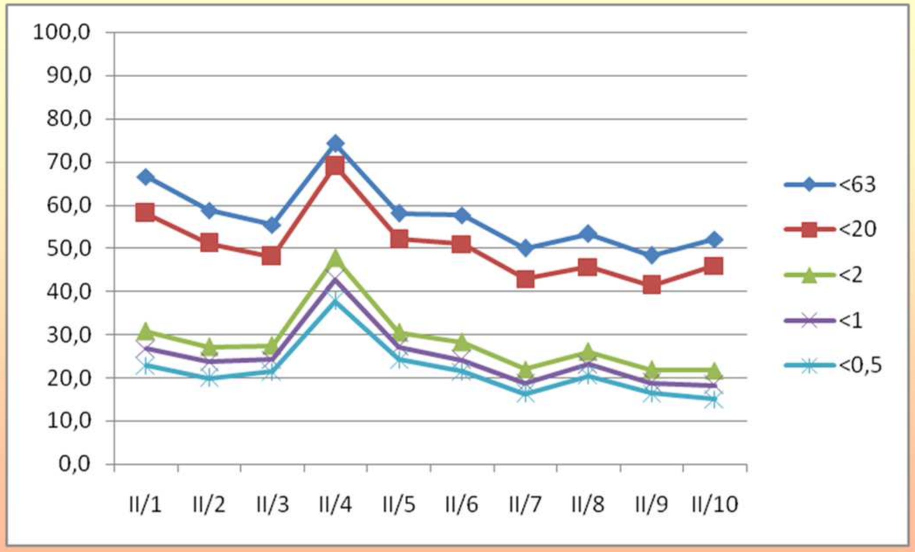
6.2 Tkemlovana

The chemical analyses

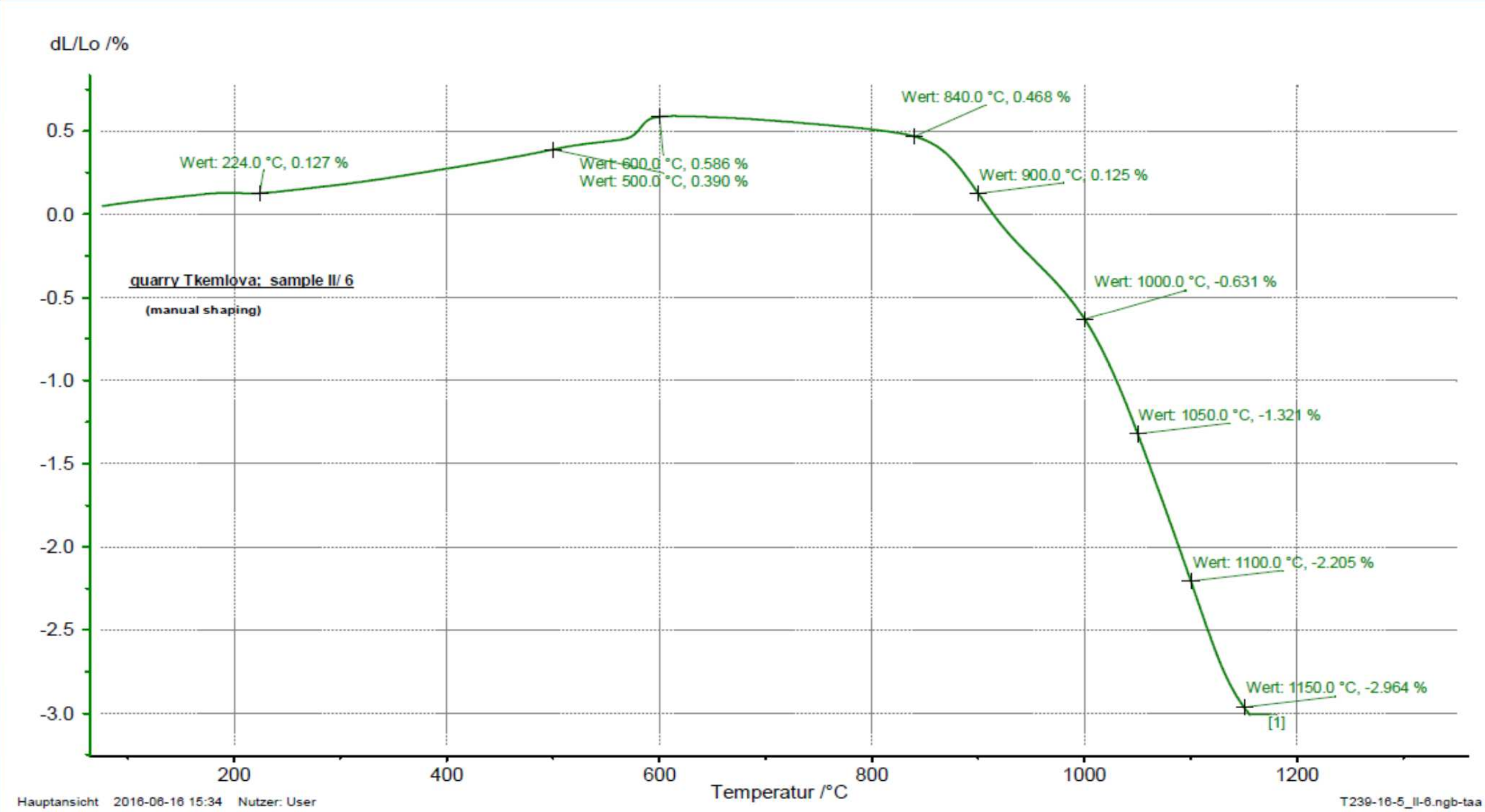
Grain size distribution

No-II
Vill. Tkemlova, Chiatura
sampling by Kapanadze Zurab

	II/1	II/2	II/3	II/4	II/5	II/6	II/7	II/8	II/9	II/10	Std_var
<63	66,5	58,8	55,4	74,2	58,0	57,7	50,0	53,3	48,3	52,1	7,8
<20	**58,1**	**51,1**	**48,0**	**69,0**	**52,0**	**51,0**	**42,9**	**45,7**	**41,4**	**46,0**	8,1
<2	**30,7**	**27,1**	**27,4**	**47,7**	**30,5**	**28,3**	**22,0**	**26,0**	**21,9**	**21,7**	7,6
<1	26,8	23,6	24,2	42,7	27,1	24,1	18,6	23,1	18,8	18,2	7,1
<0,5	22,8	19,9	21,4	37,7	24,2	21,5	16,3	20,5	16,5	15,1	6,4



6.2 Tkemlovana Thermal behavior



Gerät : NETZSCH DIL 402 C — Datei : C:\NETZSCH\Proteus61\data\T239-16-5_II-6.ngb-dle

Projekt :	Dr. M. Uebel/ GIZ Georgia	**Probe/Vorkraft :**	sample II/ 6, 25.58 mm / 25 cN	**Segmente :**	1/1	**Tabelle des Kalib.stds. :**	Al2o3ne.scl
Datum/Zeit :	14.06.2016 14:52:29	**Material :**	Ton, roh	**Modus /Messtyp :**	Standardausdehnung/Probe + Korrektur	**Material des Kalib.stds. :**	Al2O3
Labor :	KI - physik. Labor	**Atmosphäre :**	<kein Gas>/---	**Probenhaltertabelle :**	Al2o3ne.scl	**Korr./Bereich :**	820/5000 µm
Operator :	Dr. Maren Uebel	**Tempkal. Datei :**	TCALZERO.TMX	**Probenhaltermaterial :**	Al2O3		
Proben-ID :	T239-16-5_II-6	**Bereich :**	26.0°C/5.0(K/min)/1200.0°C	**Kalibrierdatei :**	E1200_5K_EAA oSTC-110615.ngb-cle		

6.2 Tkemlovana

The chemical analyses

Thermal behavior [graphs 4…6]

- That means, the coarse percentages in this quarry are in majority caused by the feldspar minerals.
- The beginning of sintering was measured of about 825…860°C and goes on continuously until the end of measurement at 1150°C.
- The measured firing shrinkage values at 1150°C are in a range from (only!!) 2,73…4,95%.

DasKeramikinstitut

6.2 Tkemlovana

The chemical analyses

Thermal behavior [graphs 4…6]

dilatometrical firing shrinkage [%]

	Sample II/ 4	Sample II/ 6	Sample II/ 10	Tkemlova
1000°C	1,63	0,63	+ 0,44	0,53
1050°C	2,61	1,32	0,14	1,26
1075°C				1,76
1100°C	3,93	2,21	1,22	
1150°C	4,95	2,96	2,73	

6.2 Tkemlovana

<u>Ceram-technological tests of specimens from quarry Tkemlovana</u>

- The specimens from extrusion didn't show cracks.
- For them a correct measurement of dry shrinkage and dry bending strength was accomplished.

- The average value of **dry shrinkage for samples Tkemlovana is → 5,8%** (30 single data; [table 14]). This is a relatively high value, but possible to control.

- The average value **of dry bending strength for samples Tkemlovana is → 10,5 MPa** (10 single data; [table 15]). This value is very high for an unfired clay body and allows a good handling without danger of demolition.

6.2 Tkemlovana

	water absorption [%]	open Porosity [%]	bulk density [g/cm³]
sample II/ 4	10,88	21,80	2,00
sample II/ 6	15,08	28,55	1,89
sample II/ 10	15,09	28,14	1,87
Tkemlovana (orig)	18,13		

Very high values of water absorption mean that the fired body is not dense in result of firing process at a maximum temperature of 1000°C. Contrariwise there is a high open porosity. So in this state it is necessary to accomplish a surface finish to realize a pore blocking for a dense Qvevri.

6.2 Tkemlovana

Ceram-technological tests of specimens from quarry Tkemlovana

- measurement was the measurement of → acid solution of the fired body from Tkemlovana
- This test was accomplished by imitation of a regular test by using a chemical acid.
- The test was carried out by using the original Georgian wine. It was the aim to prove all wine solvable components of the Tkemlovana Qvevri in fired state.

- **wine soluble percentage of the fired Qvevri Tkemlovana: → 0,04 mass % 20 grams/ 1000 litre**

6.2 Tkemlovana

- **wine soluble percentage of the fired Qvevri Tkemlovana: → 0,04 mass % 20 grams/ 1000 litre**

Protocol of Analysis: TKEM, burned

Our Sample-No. 219/05/16 KT: 231/16G
Method: XRF-Analysis according to DIN 12677
Customer: GIZ Georgia
Arrival: 4/6/2016
Sampling: by costumer, date unknown

Chemical analysis of dried sample

	mean val.	standard deviation
	weight%	weight%
SiO2	66,82	0.2
Al2O3	18,21	0.2
Fe2O3	7,80	0.02
TiO2	0,91	0.02
CaO	0,71	0.02
MgO	1,85	0.02
K2O	2,64	0.02
Na2O	0,62	0.02
BaO	0,10	0.02
ZrO2	0,04	0.02
HfO2	<0.02	0.02
SrO	<0.02	0.02
ZnO	<0.02	0.02
MnO2	0,06	0.02
Cr2O3	0,02	0.02
V2O5	0,03	0.02
P2O5	0,06	0.02
LOI 1000 °C	0,10	0,02

ff1_schmAl

6.3 Satsable

<u>Mineralogical analyses [table 17a…c]</u>

- quarry with complete other composition of hard materials
- **only quartz** (34…41%) and **no feldspar**!
- the composition of clay minerals differs to the other quarries too
- total percentage of clay minerals: 51…58%
- only 3- and 4 layer clay minerals, no Kaolinite!
- The 3 layer clay minerals dominated by Illit, what is a non swellable clay mineral but very small. This fact leads to a lot of consequences, see below.
- The ability of shaping Qvevris is positive supported by the present of 5…7% swellable clay minerals.
- 4-layer clay minerals: 6…9%.
- uniform 6% Goethite (red firing color)

DasKeramikinstitut

6.3 Satsable Mineralogical analyses

Protocol of Analysis: Pr. III; 5

Company: Keramik-Institut; Ossietzkystr. 37a; D-01662 Meißen
Phone: +49 3521-463-510 or 515
Our Sample-No. X044/16/08
Method: X-Ray-Diffractometry (XRD)/ triple preparation
Customer: GIZ Georgia *KI 231/16g*
Arrival: 06.04.2016

Mineral Phase	mean value[1] weight%	Max-Min[2] weight%
Below all phases of standard mineral analysis are listed <u>and</u> all phases found by qualitative mineral phase analysis.		
Σ Orthoclase/Plagioclase K-Feldspar + mix crystal line, Na- to Ca-Feldspar	< 2	1
Quartz	41	2
Σ Three-sheet minerals **Sum, for details look table below	45	3
Σ Two-sheet minerals Kaolinite+Halloysite+Fireclay	< 5	3
Σ Four-sheet minerals Chlorite + Chamosite ("Fe-Chlorit")	6	2
Hematite α-Fe_2O_3	< 2	1
Calcite $CaCO_3$	< 2	1
Σ Dolomite / Ankerite $CaCO_3 \times MgCO_3 + CaCO_3 \times FeCO_3$	< 2	1
Σ Anatase / Rutil[3] TiO_2	1	1
Goethite α-FeOOH	6	1

**Three-sheet minerals		
Smectite -/ Montmorillonite-Group[4]	5	3
Mixed Layer Illite/Smectite[4]	< 5	3
Illite (Hydromuscovite)[6]	36	3
Muscovite (Mica's, Sericite)	4	3
Corrensite[4,5]	< 5	3

[1] e.g. "< 2" value below LLD of e.g. 2 weight%
[2] difference between Max- u. Min-value of analysis on 3 samples
[3] TiO_2-value from chemical analysis
[4] swellable clay-minerals, [5] swellable Chlorite
[6] estimated from separately determined LOI/TOC and grain size distribution (if available)

DasKeramikinstitut

6.3 Satsable

results of chemical analyzes [table 18]

- **Fluorine, chlorine and sulfur are low**, without significant negative influence for production and environment. The element contents are similar like for the 2 other quarries [table 19].
- **content of organic carbon is high** and very different for these ten samples [table 20]. This requires a **slowly firing** during in the temperature range from 250…600°C to burn out the organic.
- Inorganic carbon wasn't detected.
- LOI of 0,30% in the fired Satsable body demonstrates a rest of organic carbon. Influences on product properties are described above (→ Vardisubani).

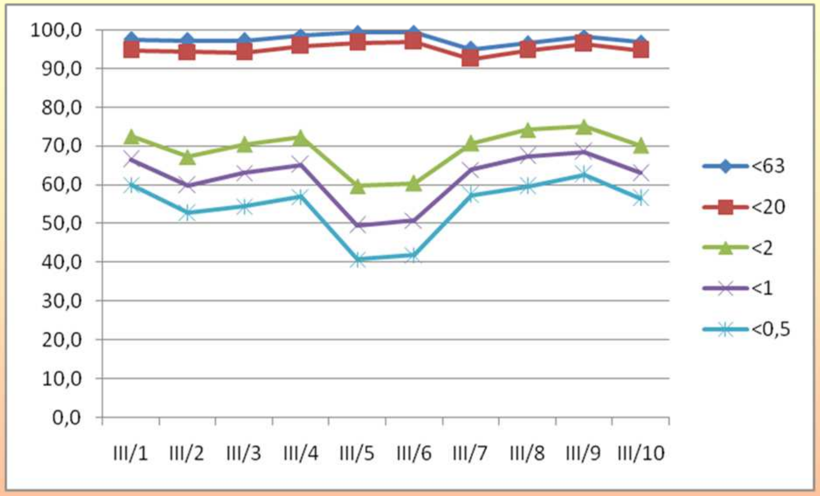
6.3 Satsable

To grain size distribution:

Satsable: a complete other characteristic → an exorbitant high fineness of the particles was measured (fine quartz, no feldspar, high percentage of clay minerals)

No-III
Vill. Makatubani, Zestafoni/
Satsable ?!
sampling by Zaliko Bojadze

	III/1	III/2	III/3	III/4	III/5	III/6	III/7	III/8	III/9	III/10	Std_var
<63	97,5	97,2	97,1	98,4	99,2	99,2	94,9	96,4	98,1	96,8	1,3
<20	**94,7**	**94,3**	**94,1**	**95,8**	**96,6**	**96,9**	**92,5**	**94,7**	**96,3**	**94,6**	1,3
<2	**72,5**	**67,2**	**70,4**	**72,2**	**59,7**	**60,4**	**70,7**	**74,2**	**75,1**	**70,2**	5,3
<1	66,5	59,9	63,1	65,1	49,6	50,8	63,9	67,4	68,5	63,0	6,6
<0,5	60,0	52,7	54,5	57,0	40,8	41,9	57,4	59,6	62,7	56,5	7,4



DasKeramikinstitut

6.3 Satsable

To grain size distribution:

- First aspect: The coarse grain, which express something to the amount of hard materials (quartz) is relatively fine (>90% are smaller than 63µm)
- Second aspect**: extraordinary fineness below 2µm →** in majority all kinds of clay minerals
- Because of this high fineness are to expect a lot of technological problems!
- **Very high dry shrinkage**

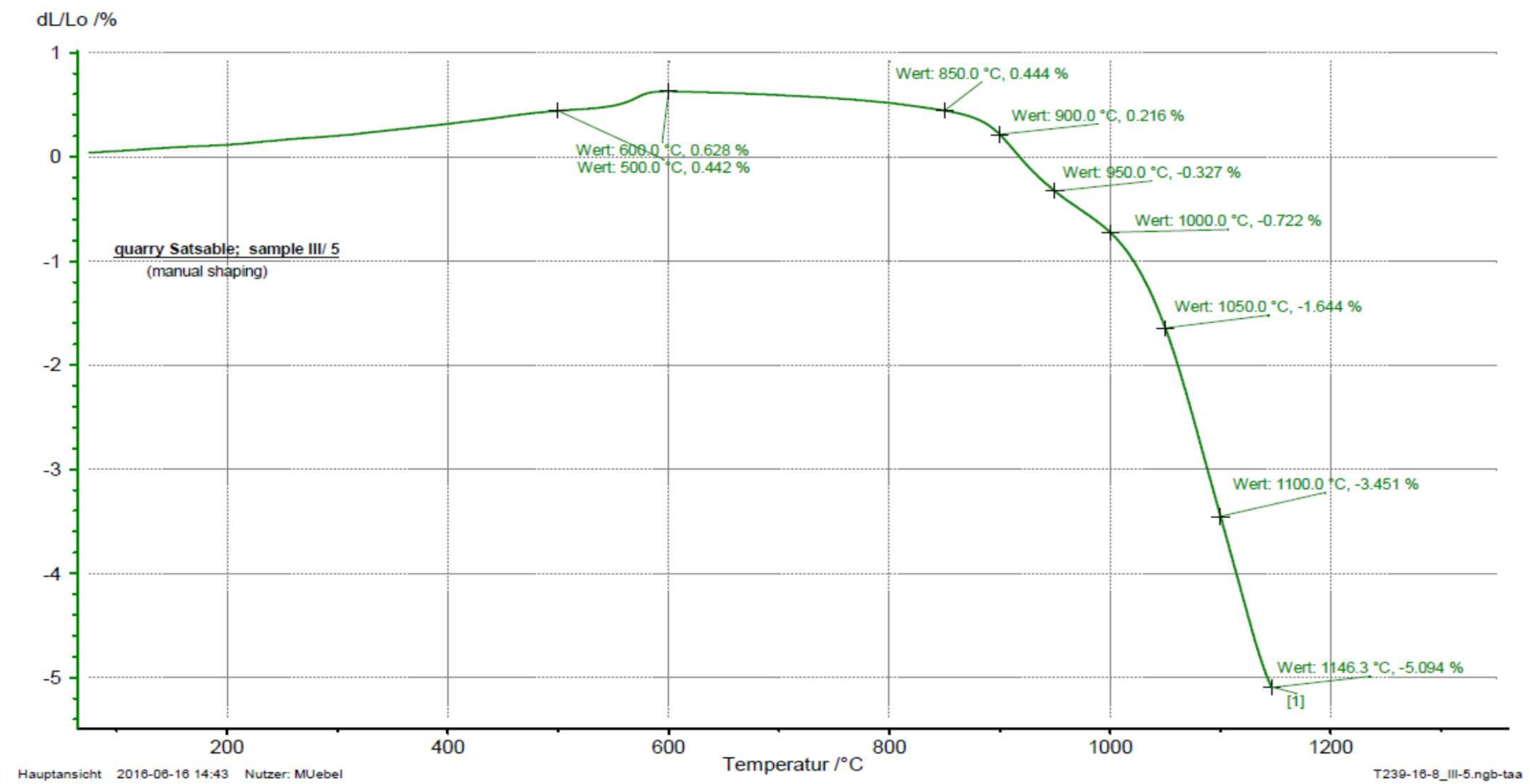
6.3 Satsable

To grain size distribution:

- tensions inside the Qvevris (tensions exist due to so called textures = preferred orientation of the clay particles in a body, because shrinkage during drying and firing is different in two directions inside the Qvevris).

- **In summary the recommendation for quarry Satsable is to mix with a coarser raw material to get more suitable properties regarding to firing of Qvevris without danger of cracks.**

6.3 Satsable Thermal behavior



Gerät : NETZSCH DIL 402 C Datei : C:\NETZSCH\Proteus\data5\T239-16-8_III-5.ngb-dle

Projekt :	Dr. M. Uebel/ GIZ Georgia	Probe/Vorkraft :	sample III/ 5, 24.80 mm / 25 cN	Segmente :	1/1	Tabelle des Kalib.stds. :	Al2o3ne.scl
Datum/Zeit :	15.06.2016 08:02:45	Material :	Ton, roh	Modus /Messtyp :	Standardausdehnung/Probe + Korrektur	Material des Kalib.stds. :	Al2O3
Labor :	physik. Labor KI Meißen	Atmosphäre :	AIR(80/20)/75	Probenhaltertabelle :	Al2o3ne.scl	Korr./Bereich :	820/5000 µm
Operator :	Dr. M. Uebel	Tempkal. Datei :	TCALZERO.TMX	Probenhaltermaterial :	Al2O3		
Versuchs-ID :	T239-16-8_III-5	Bereich :	26/5.0(K/min)/1150	Kalibrierdatei :	E1200_EAA-020913.ngb-cle		

6.3 Satsable

Thermal behavior [graphs 7-9]

- **Jump in region of quartz** transformation in the majority of the samples **not exists** → very advantageously (exceptions: samples III/5 and III/6 → higher content of quartz)
- Start of first sintering: **600°C, sinter process weakly until 900°C**
- Above 900°C: shrinkage relative strong and continuously increasing
- Because of the high fineness: reactivity of Satsable clays very high

6.3 Satsable

Thermal behavior [graphs 7-9]

dilatometrical firing shrinkage [%]

	Sample III/ 3	Sample III/ 5	Sample III/ 9	Satsable
900°C	-0,82	-0,22	-0,90	0,04
1000°C	-2,32	-0,72	-2,64	-0,62
1050°C	-3,61	-1,64	-4,21	-1,41
1070°C	-4,56	-2,31	-5,12	
1100°C				-2,54

6.3 Satsable

<u>Ceram-technological tests of specimens from quarry Satsable</u>

- The specimens from extrusion shows some small cracks too, but could measured.
- The results have to seen under this aspect!

- **average value of dry shrinkage for samples Satsable is → 7,8% (30 single data; [table 22]). This is an extraordinary high value and very difficult to control.**

- average value of **dry bending strength for samples Satsable is → 10,0 MPa** (10 single data; [table 23]).

6.3 Satsable

Ceram-technological tests of specimens from quarry Satsable

All single values are listed in [table 24].

	water absorption [%]	open Porosity [%]	bulk density [g/cm³]
sample III/ 3	11,14	23,08	2,07
sample III/ 5	14,51	27,53	1,90
sample III/ 9	3,29	7,25	2,20
Satsable (orig)	18,51		

- very high differences of the Satsable samples in dependence of their fineness → extraordinary differences are reflected in the firing result.
- Like for the other quarries the density of the sample from Georgian producer shows the lowest value. But all results show, that the range in product quality for this quarry is very wide.

DasKeramikinstitut

6.3 Satsable

- Ceram-technological tests of specimens from quarry Satsable
- measurement of → acid solution of the fired body from Satsable
- by imitation of a regular test by using a chemical acid
- by using the original Georgian wine. It was the aim to prove all wine solvable components of the Satsable Qvevri in fired state.
- wine soluble percentage of a fired Qvevri from Satsable: → 0,06 mass % 30 grams/ 1000 litre

6.3 Satsable

- wine soluble percentage of a fired Qvevri from Satsable: → 0,06 mass % 30 grams/ 1000 liters

Protocol of Analysis: SAT, burned

Our Sample-No. 219/06/16 KT: 231/16G
Method: XRF-Analysis according to DIN 12677
Customer: GIZ Georgia
Arrival: 4/6/2016
Sampling: by costumer, date unknown

Chemical analysis of dried sample

	mean val.	standard deviation
	weight%	weight%
SiO2	56,05	0.2
Al2O3	21,43	0.2
Fe2O3	11,38	0,03
TiO2	1,12	0.02
CaO	2,78	0.02
MgO	3,62	0.02
K2O	1,59	0.02
Na2O	1,25	0.02
BaO	0,06	0.02
ZrO2	0,03	0.02
HfO2	<0.02	0.02
SrO	0,02	0.02
ZnO	<0.02	0.02
MnO2	0,16	0.02
Cr2O3	<0.02	0.02
V2O5	0,04	0.02
P2O5	0,12	0.02
LOI 1000 °C	0,30	0,02

ff1_schmAl

7. Conclusions

- **So it will be helpful for a more stable production of Qvevris to consider some ceramic facts:**
- What are the statements in result of the analyses and tests in the KI?
- In general the ceramic character of each quarry is significantly different!
- A generalization isn’t possible.

8.1 Vardisubani

- **So in the sum of all minerals of the clay from Vardisubani firing at relatively low temperatures is possible, but it needs temperatures above 1125°C…1150°C for a nearly dense Qvevri**

Attention should be paid to:

- The percentage of organic substances in this quarry is very high. So in first firing step until 500°C the firing have to accomplish very slowly to give the organic time to burn out. If this isn't done, cracks in the Qvevris occur, furthermore so called black cores are created.

- Third aspect: The percentage of Quartz is very high in this quarry → strong quartz (jump) transformation with high tensions inside the Qvevris. Due to this fact the temperature region between 500°C … 620°C has to pass very slow to minimize these enormous tensions.

8.1 Vardisubani

- Fourth aspect: It would be a good idea, to grind the raw material before shaping. This would have a positive influence on sinter activity. In result lower firing temperature is necessary for the same density resp. at the same temperature it a higher density of the Qvevri's is possible.

- recommendation: For a better workability the addition of a second raw material component, which contains less hard materials, for instance a mix with a small percentage of finer clay (Satsable), would be advantage.

8.1 Vardisubani

- It would be a big step to more stability regarding to technological parameters in shaping as well as of the fired Qvevri, if at first stockpile of clay from the quarry (tonnage) is build up (in horizontal direction). In a second step this stockpile is reduced in the other direction (vertical for instance).

- The daily production should works with homogeneous mixed material.

8.2 Tkemlovana

- So in the sum of all minerals of the clay from Tkemlovana it is possible to firing at relatively low temperatures, **but it needs temperatures above 1200°C for a nearly dense Qvevri.**

- The percentage of organic substances: relatively low but existing (heating rate!)

- The percentage of quartz is relatively low in this quarry → extraordinary low heating rate in the temperature range 500°C…620°C isn't required.

8.2 Tkemlovana

Attention is paid to:

- Material from Tkemlovana is too coarse!! (2µm: 20…30%)
- It would be a very good idea, to grind the raw material before shaping. This would have a positive influence on sinter activity. In result lower firing temperature is necessary for the same density resp. at the same temperature a higher density of the Qvevri's is possible.
- To get a better workability of the raw material from Tkemlovana, the addition of clay with less hard materials inside, is advantage. (Satsable) .

8.2 Tkemlovana

Attention is paid to:

- It would be a big step to more stability regarding to technological parameters in shaping as well as of the fired Qvevri, if at first stockpile of clay from the quarry (tonnage) is build up (in horizontal direction). In a second step this stockpile is reduced in the other direction (vertical for instance).

- The daily production should work with homogeneous mixed material.

8.3 Satsable

- relatively low variation of properties, exceptions: sample III/5 and III/6
- middle content of hard material
- only quartz in a conspicuous high fineness; no feldspar minerals
- The sum of clay minerals is middle to high. The high plasticity of the Satsable material is given especially by the swellable 3 layer clay minerals and in general due to fineness of the clay in this quarry
- So in the sum of all minerals of the clay from Satsable it is possible to firing at relatively low temperatures. In the majority less than 1100°C could be enough to get a dense fired Qvevri.

DasKeramikinstitut

8.3 Satsable

Attention should be paid additionally to:

- The percentage of organic substances in this quarry is middle high. So in first firing step until 500°C the firing have to accomplish very slowly to give the organic time to burn out.
- Third aspect: attention to quartz transformation (slow between 500°C … 620°C).
- **Fourth: Due to the enormous fineness of the clay Satsable a lot of technological problems like first of all cracks, already during drying (and in result of firing) are to expect. They cannot be prevent, the only possibility is to mix this very fine Satsable clay with a coarser one!!**
- It is a requirement, build up a stockpile (like described above) to get a homogeneous grain size distribution for a stable production over a certain time!

Summary to key questions:

- Food Safety: All relevant inorganic pollutants were checked regarding to their solubility in water. The pollutant contents of the clays of all 3 clay quarries were below the detection limit of the applied measuring method. **Clay minerals are safe from Food Safety point of view.**
- **The solubility of the minerals** in wine is confirmed but is relatively low and of varying composition.

- The firing technique currently used does not allow to reach temperatures necessary to sinter all the minerals in the raw materials and consequently the produced Qvevris are not dense enough. This concludes: **pots are permeable for all liquids and pots are not easy to clean and also not to keep clean easily.**

DasKeramikinstitut

Summary to key questions:

To improve the quality of the Qvevris the following aspects should be considered:

- Produce from suitable raw material mixtures, in particular considering the grain distribution.
- Stock piles to structure the homogenisation of the raw materials
- Using of fuel aggregates which allow firing under defined condition

9. Final words

All recommendations only could be a partial result. It is indispensable, to complete this research with the aim to optimize the selection of raw materials in combination with burning process.

The KI says **'Thank you very much again'** for the possibility to take part in this project, may be to get the possibility for a further cooperation in this field.