CERAMIN CONSULTING

PRELIMINARY LABORATORY EVALUATION ON GSP SAMPLE FOR CERAMIC APPLICATIONS (NOVEMBER 2011)

Introduction

This report summarizes the results of the preliminary evaluation tests made in R.M. Ricerche Minerarie s.r.l. laboratory (Lozzolo, Italy) on 1kg of a GSP sample.

These preliminary analysis want to understand the potential of this raw material in industrial ceramic applications.

Considering that the sample contains an altered part easy to reduce with porcelain mortar and an hard part with the consistency of a rock.
Laboratory test will consider these two different qualities as different samples :

- Sample I (altered part)
- Sample II (hard part)

We made the following laboratory analyses :

- residue over 45 µm (on sample I only)
- M.O.R. after drying
- plasticity test with Pfefferkorn Method
- XRF quantitative chemical analysis (with L.o.I. at 1050 °C)
- XRD mineralogical analysis
- DTA/TG analysis
- firing test on laboratory muffle kiln .

1) Residue over 45 µm

200 g of Sample I were sieved with net of 0,045 µm in wet conditions after one night of rest and with the addition of sodium tripoliphosphate.
The result was : **81,1 % > 45 µm.**
This high value indicate that the pure clay part is very low.

2) M.O.R. after drying

400 g of Sample I were ground in planetary mills for 30 minutes and after the addition of 6 % of water they were sieved with 0,6 mm net.
Resulting powders were pressed at about 300 kg/cm² to obtain 5 x 10 cm samples with about 6.5 mm thickness.
Samples after one night in laboratory dryer a 110 °C still have been broken with suitable bending strength equipment.

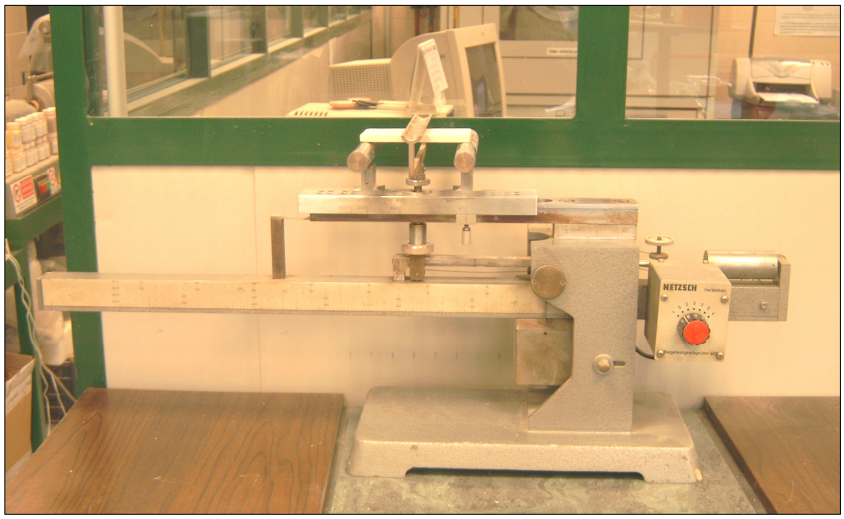


Photo n. 1 : bending strength tester

Module of rupture (M.O.R.) is calculated with the following formula :.

$$M.O.R. = \frac{3 \times F \times d}{2 \times b \times h^2} \quad [\ kg/cm^2 \text{ or } N/mm^2\ ]$$

where :

F = applied load (in kg)
d = distance between knives (in cm)
b = sample width corresponding to rupture section (in cm)
h = sample thickness corresponding to rupture section (in cm)

The average M.O.R. value was the following one :

	(kg / cm²)	(N / mm²)
Sample I	**15.1**	**1.54**

This value is considered very low for a clay utilized in ceramic tile production.

3) Plasticity test with Pfefferkorn Method

To verify the workability of Sample I we used Pfefferkorn plasticity tester.

Photo n. 2 : Pfefferkorn plasticity tester

The measurement is based on the falling of a calibrated plate on to an underlying test body, which has previously been shaped using the special forming tool provided with the instrument.
The test is made with samples prepared with different water content.
On a diagram are recorded on x axis the ratio between the height of the sample before ad after the plate falling (h/h1=a); on y axis are recorded the moisture values measured on the same samples.
The intersection point between the measured line and the value a = 3,33 indicates the moisture value that is considered as plasticity coefficient.

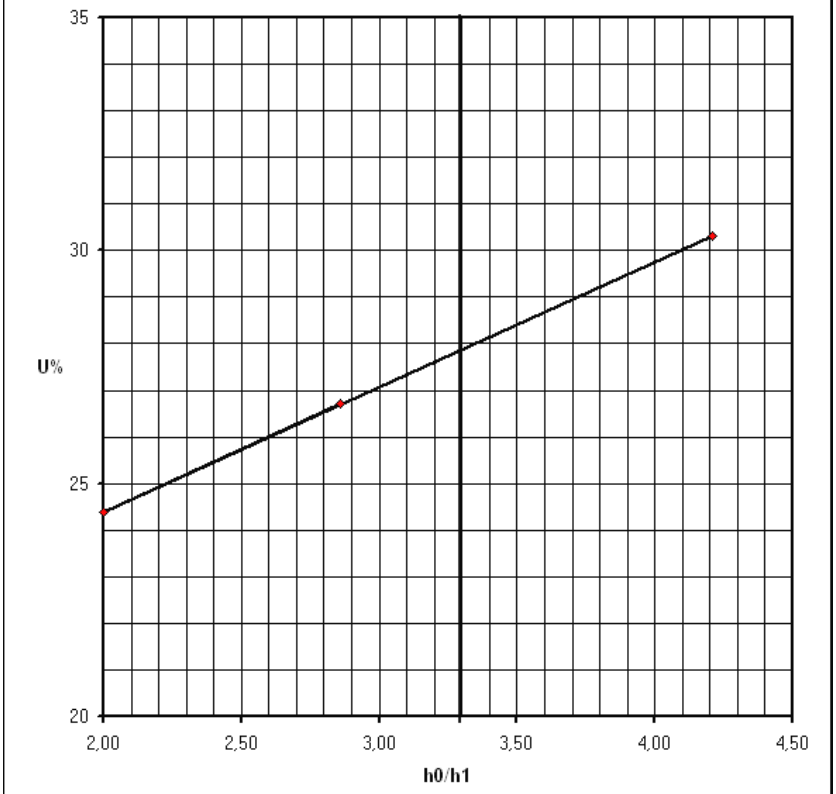
The table indicates the different grades of plasticity in Pfefferkorn test.

18 - 22	Low
22 - 26	Medium – Low
26 - 30	Medium
30 - 34	Medium - High
More than 34	High

The following table show the results of the test made on the Sample I.

Pfefferkorn plasticity test

Raw material name			Sample I			
h0/h1	2,86	2,00	4,21			
U%	26,7	24,4	30,3			



Pfefferkorn number : **27,8**

The obtained value (P.I. = 27,8 % show a medium Pfefferkorn index value that indicate a good workability and plasticity.

4) EXRF quantitative chemical analysis

The chemical analysis were made with EDXRF spectrometer Ametek Spectro IQ II.

Photo n. 3 : X ray instrument EDXRF Ametek Spectro IQ II.

Chemical analysis were made on tablets obtained mixing 10 g of micronized powder of each raw material and 2.5 g of Licowax C Micropowder PM, used as binder.
Such mixtures have been therefore pressed with specific pressure about 2000 kg/cm².
All the samples tested were analysed in the same laboratory conditions and with suitable standard procedures.
The loss of ignition was calculated after a firing test on laboratory muffle kiln with a three hour cycle at 1050°C and with 1 hour at the maximum temperature.

The results are synthesized on the following table :

Name Oxide	**Sample I** **(altered part)** %	**Sample II** **(hard part)** %
SiO_2	**74,3**	**74,0**
Al_2O_3	**14,6**	**14,5**
Fe_2O_3	**0,60**	**0,64**
TiO_2	**0,43**	**0,48**
CaO	**0,45**	**0,25**
MgO	**0,74**	**0,57**
Na_2O	**0,61**	**3,09**
K_2O	**3,93**	**2,95**
SO_3	**0,57**	**0,30**
P. F.	**3,53**	**2,82**

5) XRD Qualitative mineralogical analysis

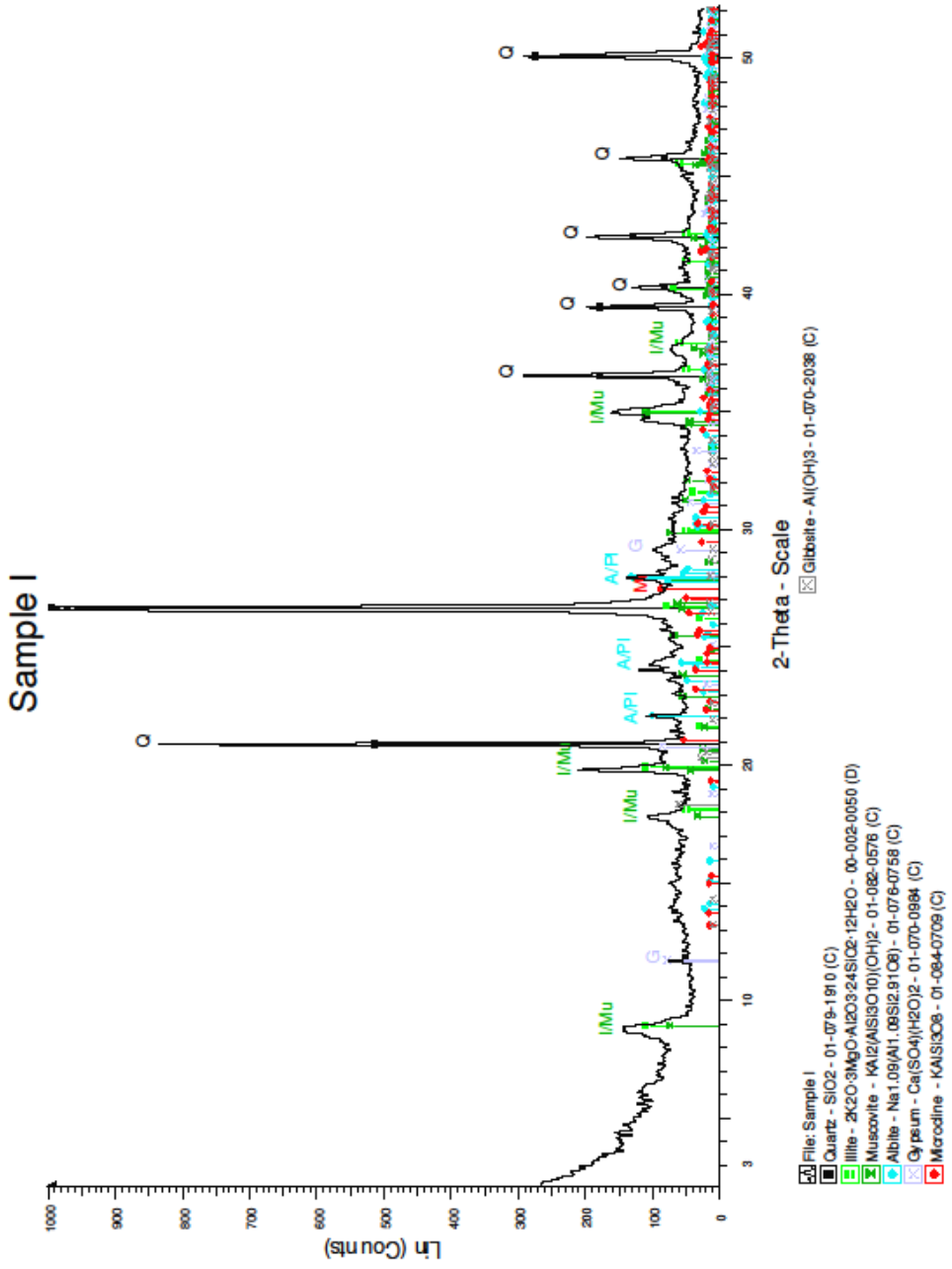
The mineralogical analysis were made with X-ray diffractometer 5000D Bruker Axs (Siemens).

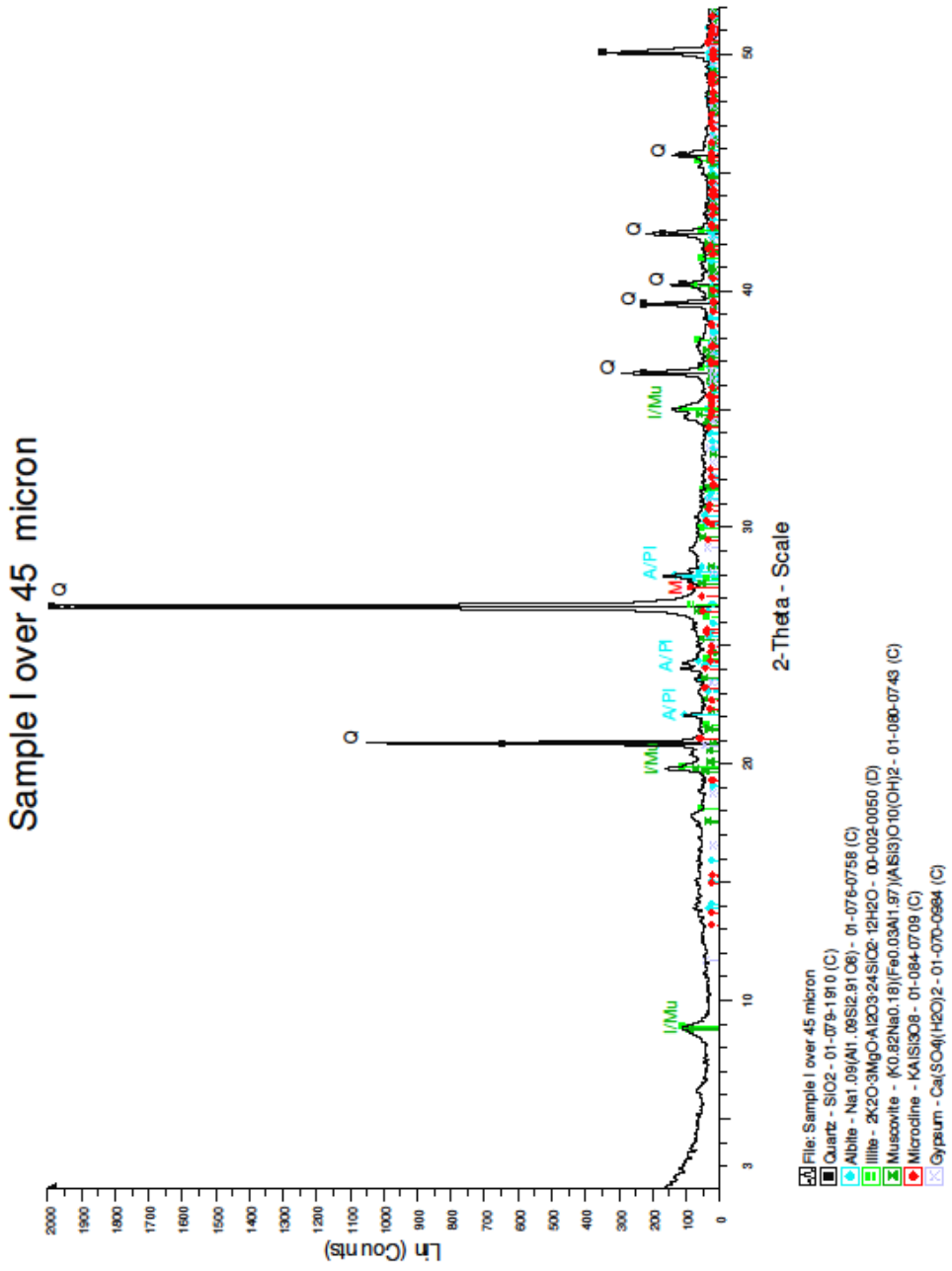
Photo n. 4 : X ray diffractometer 5000 D Bruker AXS.

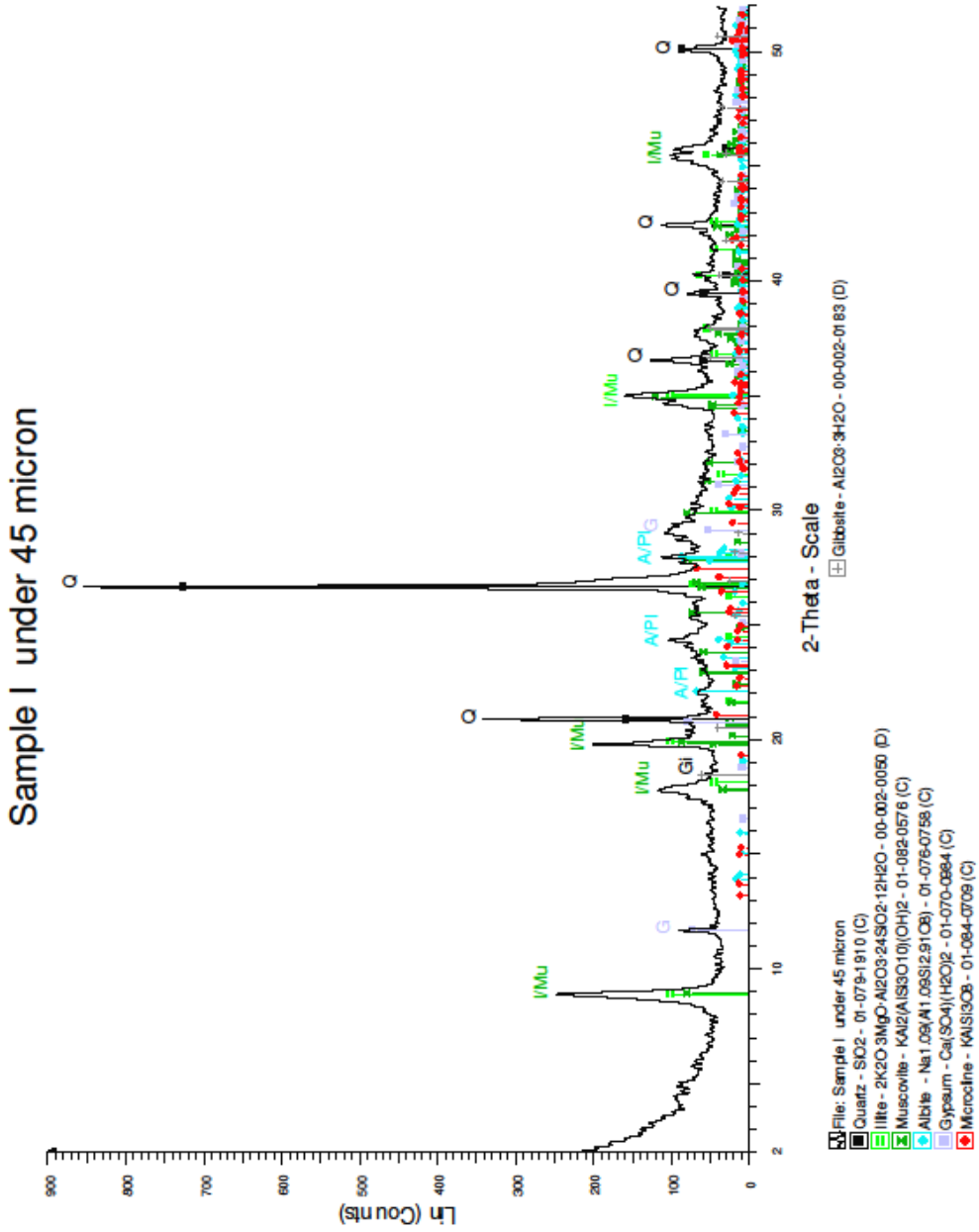
For the qualitative evaluation it was utilized PDF2 (Powder Diffraction File) database standards by JCPDS-ICDD (Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data).

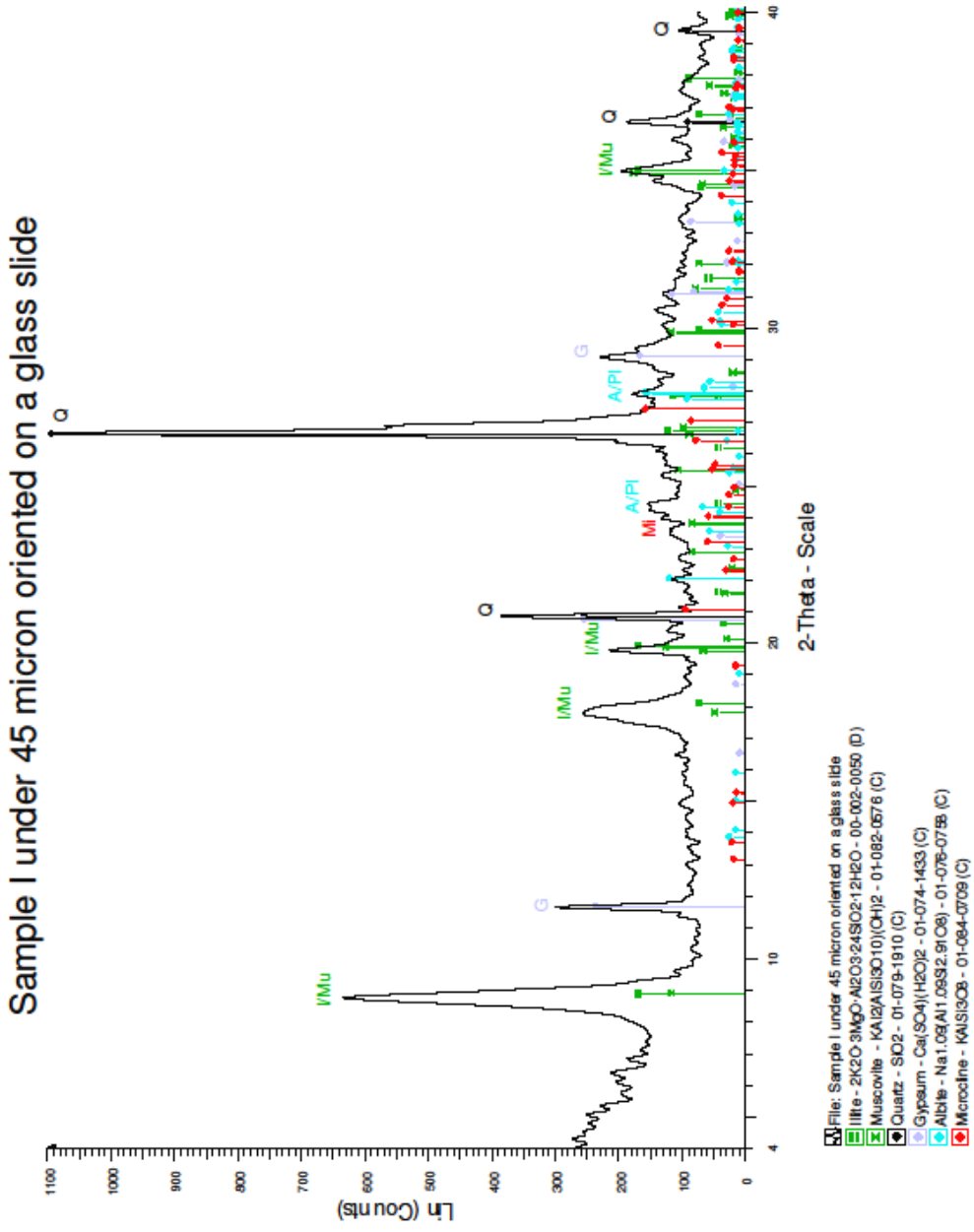
The XRD analysis were made also on Sample I > 45 µm, Sample I < 45 µm and Sample I < 45 µm oriented in wet conditions on a glass slide.

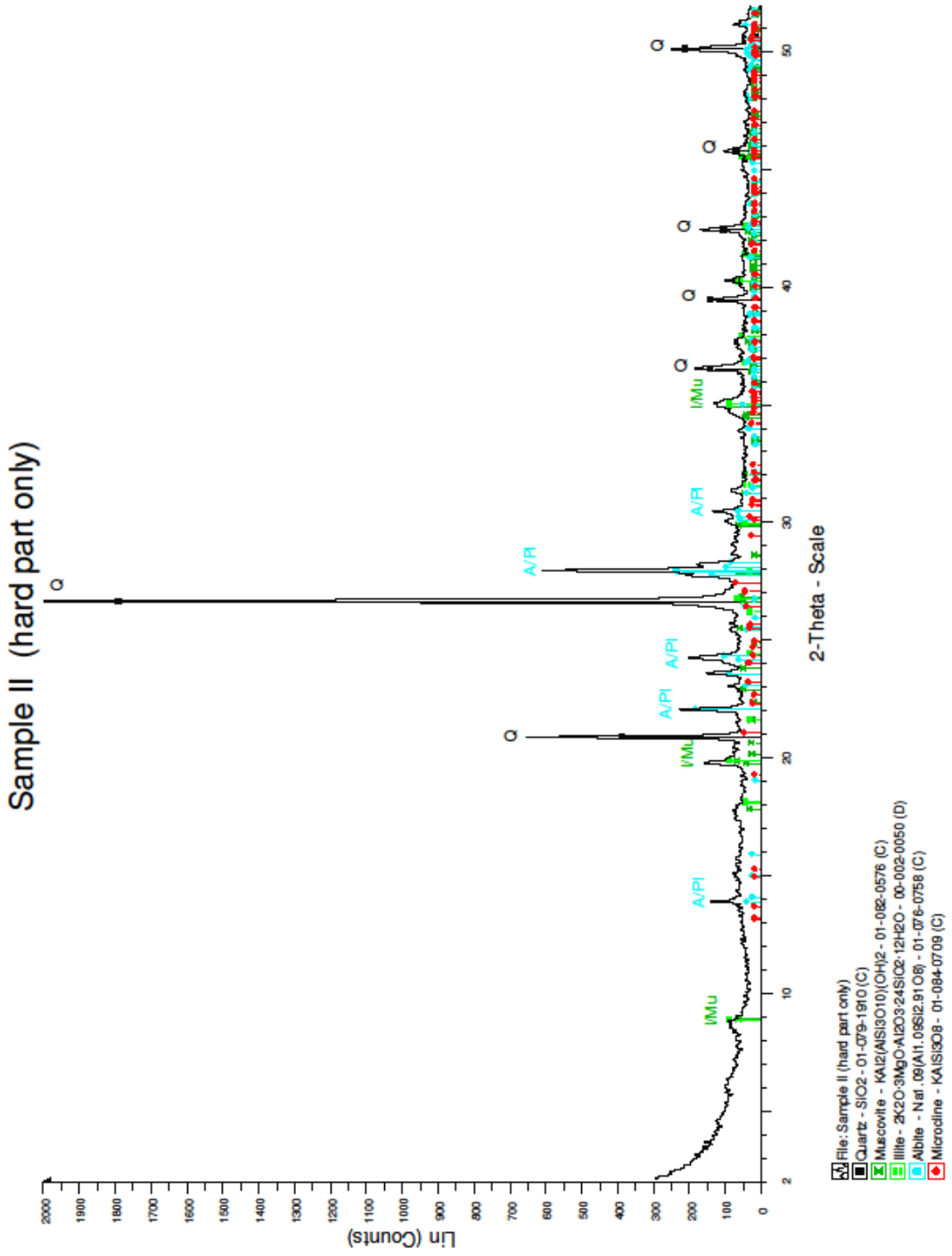
In the following pages are attached all the diagrams and their interpretation.

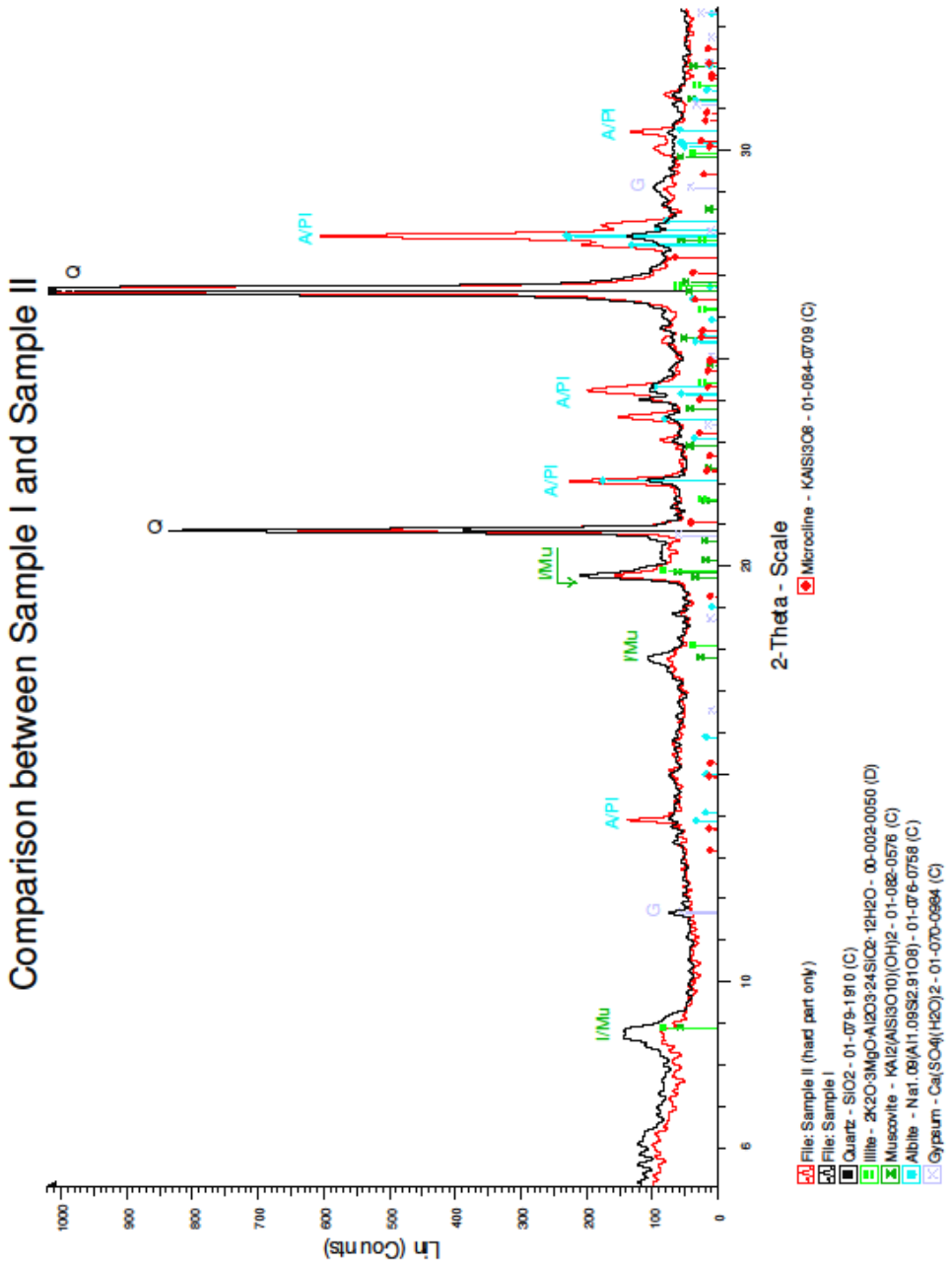

Sample I
Ln (Counts)
2-Theta - Scale
Gibbsite - Al(OH)3 - 01-070-2038 (C)
File: Sample I
Quartz - SiO2 - 01-079-1910 (C)
Illite - 2K2O·3MgO·Al2O3·24SiO2·12H2O - 00-002-0050 (D)
Muscovite - KAl2(AlSi3O10)(OH)2 - 01-082-0578 (C)
Albite - Na1.09(Al1.09Si2.91O8) - 01-076-0758 (C)
Gypsum - Ca(SO4)(H2O)2 - 01-070-0984 (C)
Microcline - KAlSi3O8 - 01-084-0709 (C)


Sample I over 45 micron
Ln (Counts)
2-Theta - Scale
Q
I/Mu
A/Pl
File: Sample I over 45 micron
Quartz - SiO2 - 01-079-1910 (C)
Albite - Na1.09(Al1.09Si2.91O8) - 01-076-0758 (C)
Illite - 2K2O·3MgO·Al2O3·24SiO2·12H2O - 00-002-0050 (D)
Muscovite - (K0.82Na0.18)(Fe0.03Al1.97)(AlSi3)O10(OH)2 - 01-080-0743 (C)
Microcline - KAlSi3O8 - 01-084-0709 (C)
Gypsum - Ca(SO4)(H2O)2 - 01-070-0984 (C)


Sample I under 45 micron
Ln (Counts)
2-Theta - Scale
File: Sample I under 45 micron
Quartz - SiO2 - 01-079-1910 (C)
Illite - 2K2O·3MgO·Al2O3·24SiO2·12H2O - 00-002-0050 (D)
Muscovite - KAl2(AlSi3O10)(OH)2 - 01-082-0578 (C)
Albite - Na1.09Al1.09Si2.91O8) - 01-076-0758 (C)
Gypsum - Ca(SO4)(H2O)2 - 01-070-0984 (C)
Microcline - KAlSi3O8 - 01-084-0709 (C)
Gibbsite - Al2O3·3H2O - 00-002-0183 (D)
Q
I/Mu
A/Pl
G
Gi


Sample I under 45 micron oriented on a glass slide
Lin (Counts)
2-Theta - Scale
Q
I/Mu
G
A/Pl
Mi
File: Sample I under 45 micron oriented on a glass slide
Illite - 2K2O·3MgO·Al2O3·24SiO2·12H2O - 00-002-0050 (D)
Muscovite - KAl2(AlSi3O10)(OH)2 - 01-082-0576 (C)
Quartz - SiO2 - 01-079-1910 (C)
Gypsum - Ca(SO4)(H2O)2 - 01-074-1433 (C)
Albite - Na1.09(Al1.09Si2.91O8) - 01-076-0758 (C)
Microcline - KAlSi3O8 - 01-084-0709 (C)


Sample II (hard part only)
Lin (Counts)
2-Theta - Scale
Q
A/Pl
I/Mu
File: Sample II (hard part only)
Quartz - SiO2 - 01-079-1910 (C)
Muscovite - KAl2(AlSi3O10)(OH)2 - 01-082-0576 (C)
Illite - 2K2O·3MgO·Al2O3·24SiO2·12H2O - 00-002-0050 (D)
Albite - Na1.09(Al1.09Si2.91O8) - 01-076-0758 (C)
Microcline - KAlSi3O8 - 01-084-0709 (C)


Comparison between Sample I and Sample II
Ln (Counts)
2-Theta - Scale
Q
A/Pl
I/Mu
G
K
Microcline - KAlSi3O8 - 01-084-0709 (C)
File: Sample II (hard part only)
File: Sample I
Quartz - SiO2 - 01-079-1910 (C)
Illite - 2K2O·3MgO·Al2O3·24SiO2·12H2O - 00-002-0050 (D)
Muscovite - KAl2(AlSi3O10)(OH)2 - 01-082-0578 (C)
Albite - Na1.08(Al1.08Si2.91O8) - 01-076-0758 (C)
Gypsum - Ca(SO4)(H2O)2 - 01-070-0984 (C)

The XRD analysis show that the samples contain the main following minerals :

- Quartz
- Illite / Muscovite
- Albite
- Gypsum

The difference between Sample I and Sample II is that the plagioclase is altered in Illite and the presence of Gypsum is more relevant.
Kaolinite, usually present, in these kind of rocks is not relevant.

6) DTA/TG analysis

The DTA/TG analysis were made with Netzsch STA 409 EP simultaneous thermal analyzer.

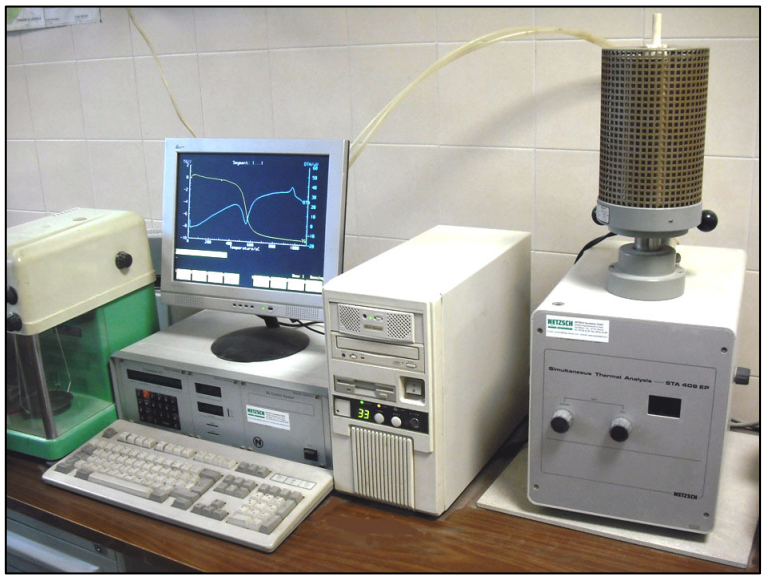
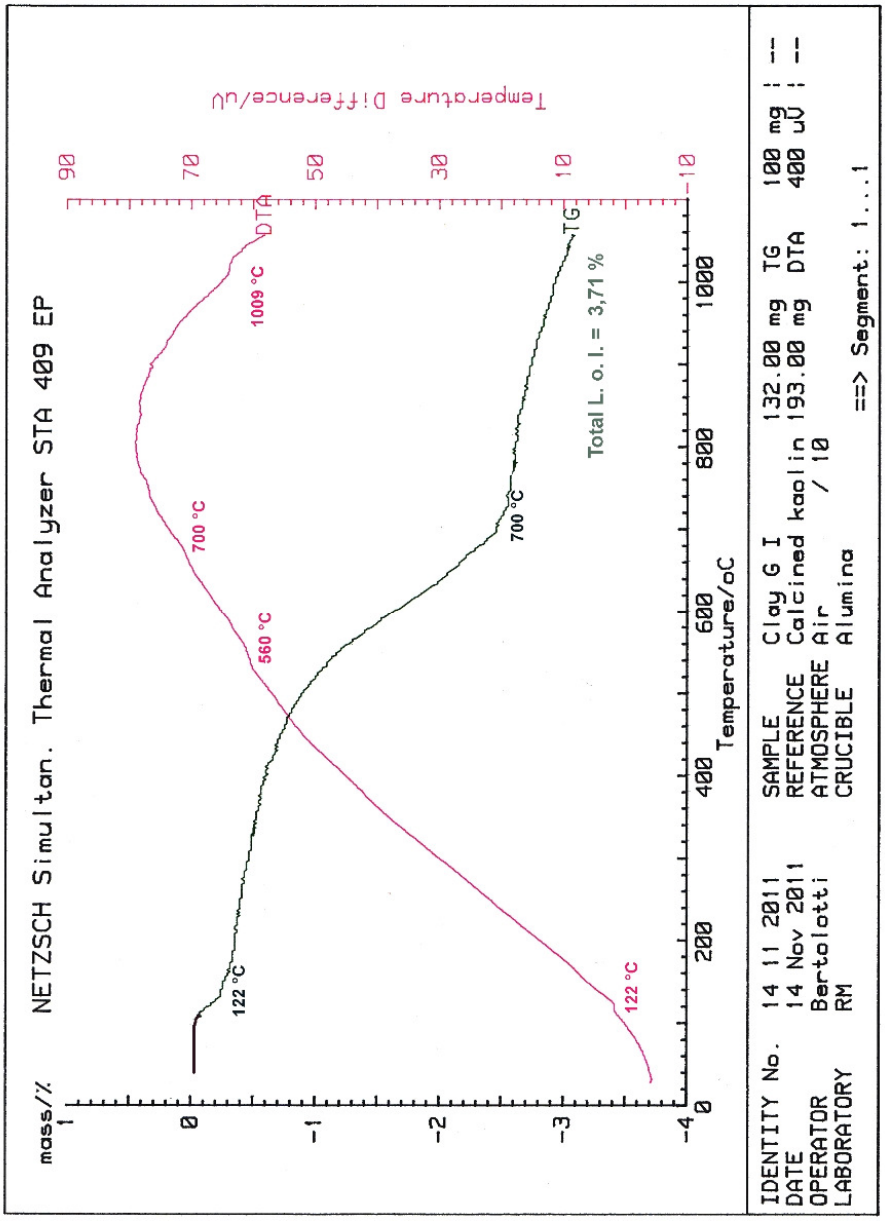


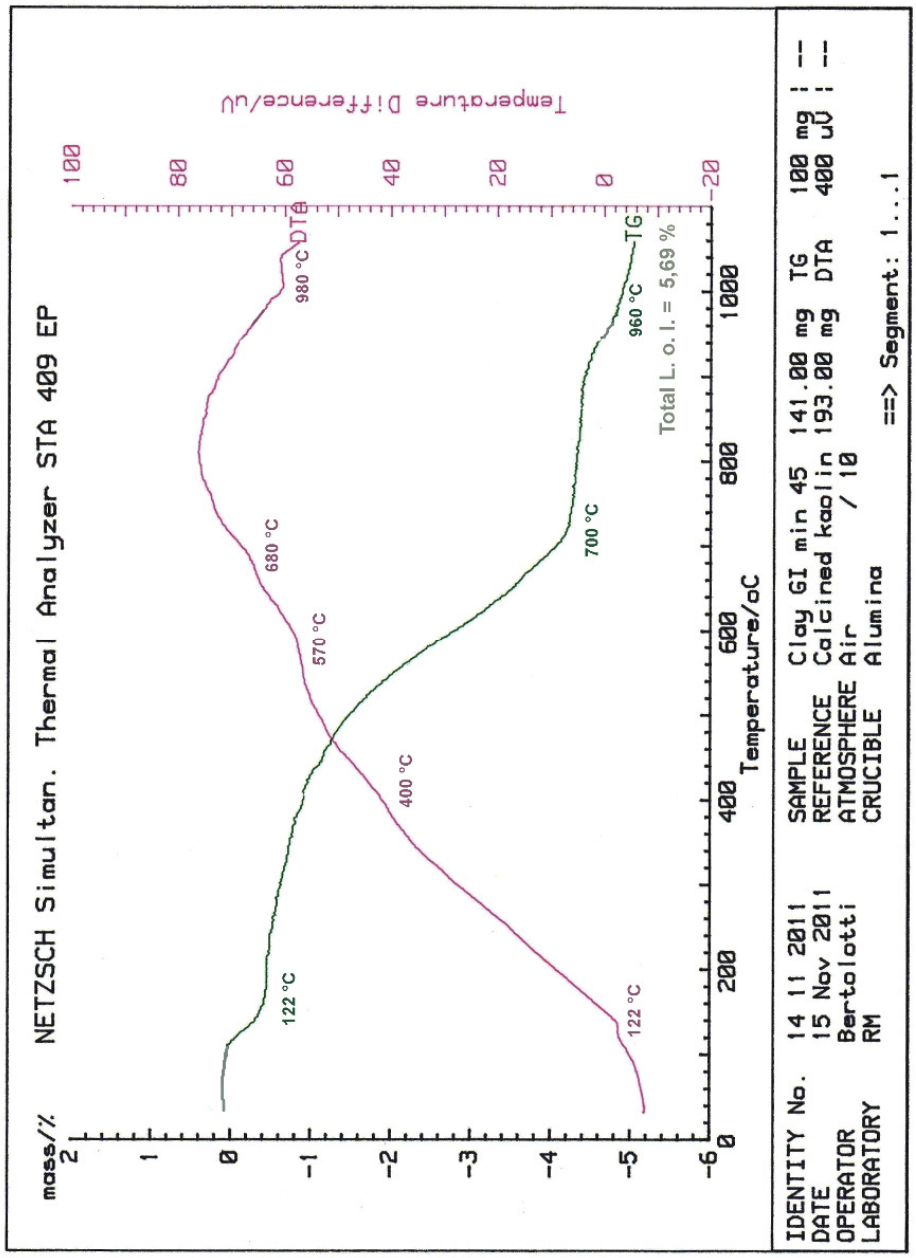
Photo n. 5 : Netzsch STA 409 EP.

The DTA/TG analysis were made only on Sample I and Sample I < 45 µm

D.T.A. diagrams show week endothermic peaks that are characteristics of Illite mineral.
The peak at 122 °C must be related to the presence of Gypsum.
T.G. diagrams show a first L.o.I. at 120 °C, an important second. L.o.I. at about 700 °C and finally a third change at 980 °C better visible on sample < 45 µm.

In the following pages are attached all the resulting diagrams.


NETZSCH Simultan. Thermal Analyzer STA 409 EP
mass/%
Temperature/oC
Temperature Difference/uV
DTA
TG
122 °C
560 °C
700 °C
1009 °C
700 °C
122 °C
Total L. o. l. = 3,71 %
IDENTITY No. 14 11 2011
DATE 14 Nov 2011
OPERATOR Bertolotti
LABORATORY RM
SAMPLE Clay G I
REFERENCE Calcined kaolin
ATMOSPHERE Air / 10
CRUCIBLE Alumina
132.00 mg TG 100 mg ; --
193.00 mg DTA 400 uV ; --
==> Segment: 1...1


NETZSCH Simultan. Thermal Analyzer STA 409 EP
mass/%
Temperature/oC
Temperature Difference/uV
DTA
TG
980 °C
960 °C
680 °C
570 °C
400 °C
700 °C
122 °C
122 °C
Total L. o. I. = 5,69 %
IDENTITY No. 14 11 2011
DATE 15 Nov 2011
OPERATOR Bertolotti
LABORATORY RM
SAMPLE Clay GI min 45 141.00 mg TG 100 mg
REFERENCE Calcined kaolin 193.00 mg DTA 400 uV
ATMOSPHERE Air / 10
CRUCIBLE Alumina
==> Segment: 1...1

7) Laboratory muffle kiln firing test

The micronized powder of G I and G II sample already prepared for all the other analyses was also utilized to prepare round samples pressed at 400 kg/cm².

These samples were fired in laboratory muffle kiln with cycle of five hours at the temperature of 1220 °C with 15 minutes at the maximum temperature.

Photo n. 6 and 7 : laboratory muffle kiln

On the following page we attached data sheet with firing test results.

Firing test on laboratory muffle kiln Cycle : 1220 °C 5 hours with 15 minutes at the max. T. (Temperature Buller ring 75 = 1200 °C)	
Sample I	**Sample II**
	
Water absorption (%) **0,47**	Water absorption (%) **0,15**
Total shrinkage (%) **4,44**	Total shrinkage (%) **in expansion**
Colour **LIght grey**	Colour **Light grey**

The samples after the firing test look very clear and show a low water absorption. Sample II is already in expansion after reaching W.A. = 0 %.

Conclusions

The results of the preliminary analyses made on GSP sample (divided as Sample I and Sample II) underline a raw material surely interesting for ceramic applications.

Positive elements found in laboratory tests are :

- raw material easy to crash and grind in laboratory mills
- good plasticity with Pfefferkorn method (P. I. = 27,8)
- low F_2O_3 and TiO_2 content if consider the material as a clay
- presence of Illite mineral in clay part and Na feldspar
- good melting behaviour at 1200 °C (< 0,5 % water absorption)
- light colour of the material after firing

Negative elements found are the following ones :

- low presence of clay fraction in the sample (81,1 % > 45 µm) and presence of rock parts with different chemical and mineralogical composition
- low M.O.R after drying (less then 20 kg/ cm² or 2 N/mm²)
- high iron F_2O_3 and TiO_2 content and low Na_2O content if consider the material as a feldspar
  (usually Turkish feldspars have F_2O_3 = 0,1-0,2 % and Na_2O = 9 %)
- presence of SO_3 (> 0,5 % in Sample I)
- very low presence of kaolinite

To confirm the general positive preliminary evaluation of this raw material it must be done a detailed geological study of the deposit to understand if it's possible to select the fine and the hard quality as two different materials. It's also important understand if the alteration grade of the mother rock is always the same or if it's only at the surface of the material. For this reason boreholes will help to understand better the potentiality of the deposit.

To introduce this material in the ceramic international market is also important to have and idea of a preliminary FOB and CIF price (starting for example to consider a boat of 3000 tons).
I also suggest to study the possibility to supply this material in Iranian ceramic market moving the material by trucks. In Tehran area there are many important ceramic factories.
Regarding Turkey ion the contrary this material in my opinion is not very interesting.

Best regards.

Arona, 24 November 2011

Gian Paolo Bertolotti