

X-ray fluorescence (XRF)

Laboratory:

n.4 3D microtomographic systems,

n.2 portable XRF systems

Various X-ray detectors: HpGe, SI-PIN, SDD, NaI.

n. 6 X-Ray tubes

Four samples of mineral of different colors as representative of the mural decorations have been collected at the quarries. Then, they are pressed in pellet. Latter operation is important to obtain a smooth surface to be analyzed with X-Ray diffraction (XRD). This operation is not required in a XRF setup. It is based on a X-ray tube with Ag anode operating up to 50 kV, 80 μ A, a SDD detector with a DSP based multichannel analyzer both by Amptek. It is possible to put a capillary optics in front of detector in order to analyze a small area of the sample (about 100 μ m wide). However, in this case the number of count per seconds is very low and so the measurement time long. The system is connected to a notebook with the Monte Carlo code inside. Depending from the configuration, the Monte Carlo code can produce a high quality simulation of the experimental spectrum in 3-5 minutes, i.e., the same time required by a measurement, allowing one to make a quantitative determination of the chemical contents almost in real time. The quality of the fit can be consider higher than a conventional background-peak fit performed by all the quantitative well-known softwares, such as Axil or PyMCA, as visible in figure 2. Moreover, as mentioned before, influence of roughness surface can be introduced at the run time. This is the case of untreated samples while in the case of pressed pellet the surface can be considered as smooth.

In figure 1 the XRF spectra of the samples M1 are shown. The two spectra are almost coincident except for the Nb contents, that can be used as a marker. Both the samples contain Fe, Ti, Mn, Sr,Zr, Cr, Ca and As, while only M1 sample from site 1B contain Nb. In figure 2, the monte carlo fit is depicted superimposed to M1.

In figure 3 three X-Ray spectra from M2 samples are shown. In this case the elemental contents of the two M2 samples are the same with no exception. The main elemental content is formed by S, Ca, Ti, Fe, Zn, As, Br and Sr with traces of rare earth elements. In table I the quantitative results of the two kind of samples is reported.



A portable XRF system (1-2-3 SDD with miniX X-ray tube by Amptek). Sample: a peregrine flask

Figure 1

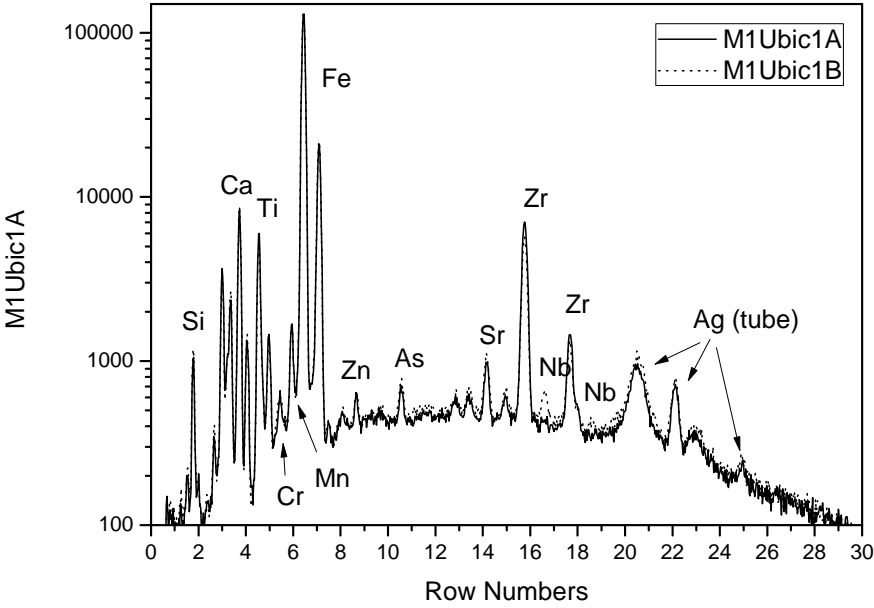


Figure 2

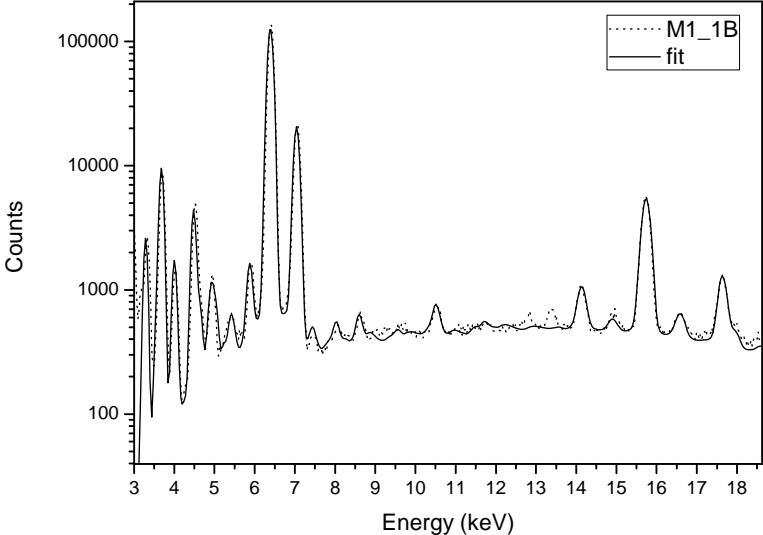


Figure 3

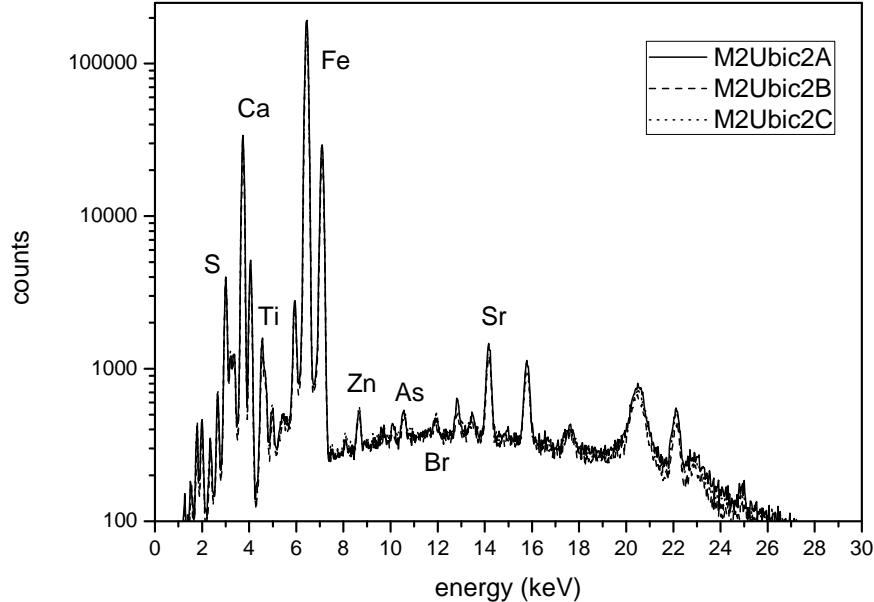


Table I

M1 1B									
K	CA	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As
1.5	3	0.6	0.02	0.08	8	0.01	0.01	0.02	0.03
Sr	Y	Zr	Nb	La	Ce	Pr			
0.06	0.01	0.6	0.03	0.2	0.05	0.05			

M2									
K	CA	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As
1.5	3	1	0.02	0.08	8	0.01	0.01	0.02	0.02
Sr	Y	Zr	Nb	La	Ce	Pr	Sm		
0.06	0.02	0.9	0	0.2	0.05	0.05	0.01		

X-ray diffraction (XRD)

(laboratory: <http://chimica.uniss.it/ws.php?mod=researchgroups&grpid=418>)

The examined samples were coded as it follows:

Index	Labelling
1	M1 Ubicacion 1A
2	M1 Ubicacion 1B
3	M2 Ubicacion 2A
4	M2 Ubicacion 2B
5	M2 Ubicacion 2C

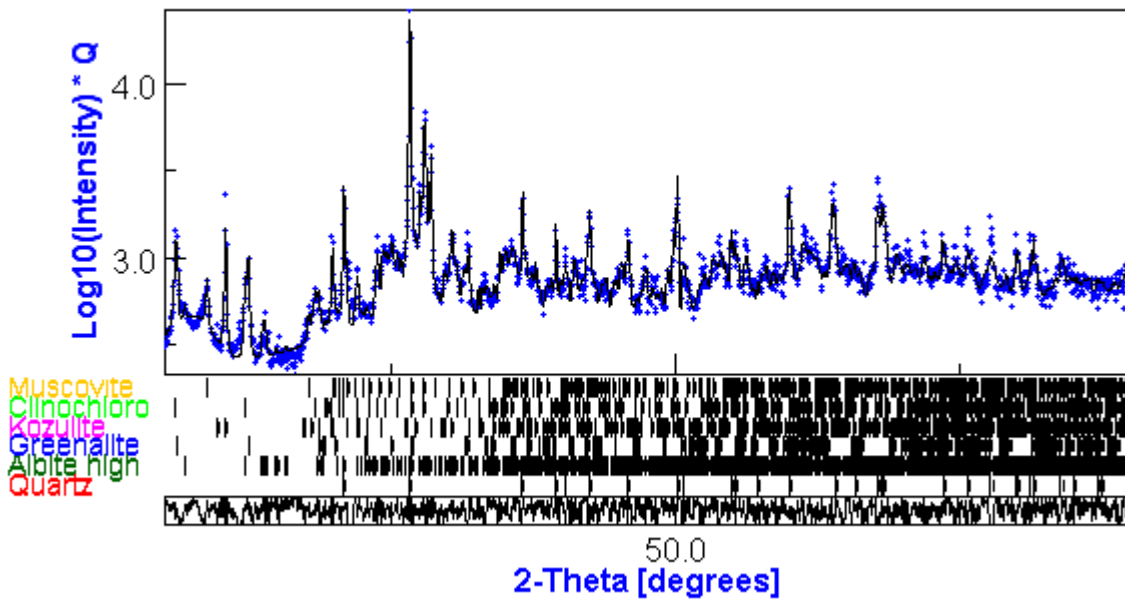
Powder X-ray Diffraction patterns were collected using a Bruker D8 powder diffractometer in the Bragg Brentano geometry with 0.5° divergence-antiscatter slits in the angular range from 5 to 90° in 2θ , using Cu $K\alpha$ radiation fed by a generator working at a power of 40 kV and 40 mA □

The digitized spectra were collected overnight and the phase analysis conducted using the X'Pert HighScore software RM, which attributes the phases on the basis of an automatic “search & match” approach. The phases were further validated and quantitatively evaluated through the Rietveld method, as it will be shown below.

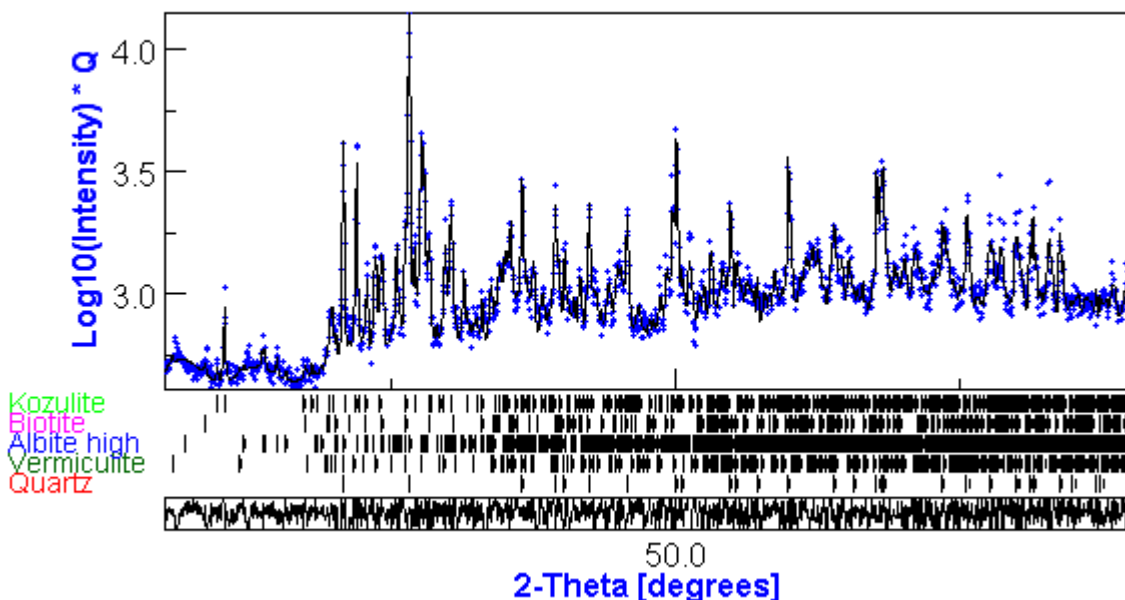
In Figure 1 we show the pattern of Specimen M1 Ubicacion 1A which appears typical of ground material. Actually a phase analysis by the search-match method reveals that it is composed mainly by the plagioclase phase particularly similar to albite (triclinic) accompanied by microcrystals of quartz. The low angle peaks permit the attribution of muscovite/illite phase (nearly with the same diffraction pattern), as well as non-negligible contributions due to clinocllore, kozulite and greenalite clay minerals. Even if the problem appears complex we have attempted a quantitative evaluation of the phases that must be managed with caution, allowing a realistic uncertainty, being this a pilot case in applying the Rietveld protocol.

The following data were obtained ($\pm 10\%$ of their value):

Quartz (SiO₂) 28 wt%; Albite 29 wt%; Muscovite 10 wt%; Greenalite 9; Kozulite 12 wt%; Clinocllore 12 wt%. Note that the clays are also reported to contain some amount of iron atoms that should also be confirmed by XRF in the joint study on the same specimens.

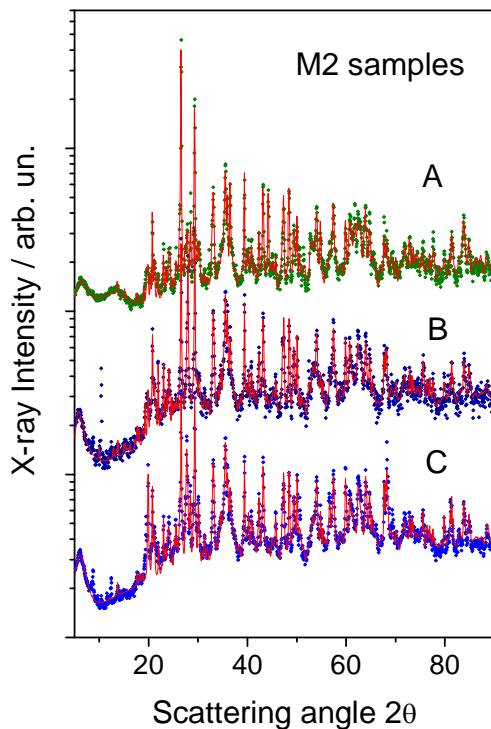


In Figure 2 we report the Rietveld analysis of the “M1 Ubicacion 1B” specimen. Again, the pattern is dominated by the presence of quartz and plagioclase (albite mineral phase). The kozulite, biotite and vermiculite phases appear to be also present. It must be kept in mind that this suggestion is supported by the ability of these phases to account closely the succession of peaks observed in the experimental pattern. In all, the albite plagioclase phase seems to be dominant being weighted at 42% wt%, followed by quartz (23 wt%), vermiculite (20 wt%), Kozulite (10%) and biotite (the remaining 5 wt%).



As it concerns the M2 series of three specimens, the situation is different and even more complex from a mineralogical perspective.

Yet some evident changes in the mineralogy point out significant differences with respect to the M1 specimens.



First the mixture are very similar among them. They contain quartz and anorthite, but also calcite and hematite (responsible for the dark-red colour) and perhaps a titanate or titanium oxide.

Here is a tentative quantitative evaluation of phases, with the obvious recommendation to keep with caution and only after crossing the data with those from X-Ray Fluorescence and other.

In the case of M2 Ubicacion 1A specimen, quartz is the main phase 43 wt%, with a significant presence of calcite 23 wt%, the plagioclase (anorthite-labradorite phase) at the level of 20 wt%; hematite 9% and goethite 3 wt%, with suspected presence of elemental iron and of LiTi_2O_4 less than 1 wt%.

For the specimen M2 ubicacion 2B, anorthite is the main phase (41 wt %) followed by Calcite (CaCO_3) present at a level of 21 wt%, then we can envisage quartz at 16 wt%, hematite at 10 wt%, kozoilite 7 wt%, goethite 4 wt% and less than 1% of LiTi_2O_4

The specimen M2 Ubicacion 2C shows a mineralogical composition close to M2-Ubicacion 2A. Our numerical Rietveld analysis suggests anorthite at a level of 49 wt%; calcite 17 wt%; quartz 15 wt%; hematite 9%; Goethite 4 wt%; muscovite 5 wt % and the titanate phase less than 1 wt%