

Bricks in historical buildings of Toledo City:

Characterization and restoration

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ABSTRACT.- Two different types of ancient bricks (XII-XIVth centuries) collected from historical buildings of Toledo (Spain) were characterized by Optical Microscopy, SEM/EDS, Electron microprobe, XRD, DTA and ⁵⁷Fe-Mössbauer spectroscopy. Physical properties such as water absorption and suction, porosity, density and compression strength were also determined. Several minerals found in the brick matrix, such as garnet, let us infer raw material sources; calcite, dolomite, illite and neo-formed gehlenite and diopside phases, on temperature reached in firing; secondary calcite, on first cooling scenarios; and manganese micro-nodules, on late pollution environments. XRD and DTA of original and re-fired samples supply information about firing temperatures. Additional data on firing conditions and type of the original clay are provided by the Mössbauer study. Physical properties of both types of bricks were compared and correlated with raw materials and fabric and firing technology employed. The physico-chemical characterization of these bricks provides valuable data for restoration purposes to formulate new specific bricks using neighbouring raw materials.

Keywords: Brick characterization; Heritage; Historical buildings; XRD; DTA; SEM; Mössbauer Spectroscopy; Optical polarising microscope, paleo-indicator, raw material provenance.

1. Introduction

During the last two decades, architectural heritage preservation has reached a rising interest for scientists, architects, engineers and archaeologists, this subject being an interdisciplinary research area. When damaged historical masonry needs to be restored with substitution bricks, a good characterization of both, new and old material lets us forecast the chemical behaviour of the system. In addition to the necessary aesthetic aspect, the familiarity with physico-chemical properties is crucial to maintain chemical equilibrium with adjoining materials. The historical understanding is not just to analyse and preserve objects but also to investigate the knowledge and skills used to produce and use them [1]. Romans, Jews, Arabs and Christians built the ancient city of Toledo (Spain) with bricks as the main construction material; nowadays, many historical monuments are being refurbished improving the regional wealth source by tourism. The main goals of the building material characterization are preservation and restoration, aiding archaeological studies which include: (i) origin of historical raw materials, (ii) processes and changes in archaeological artefacts undergone during burial, (iii) determination of original firing temperature and (iv) reconstruction of firing techniques and manufacturing technologies [2]. Bricks and ceramics can be considered as artificial rocks fired in kilns (“industrial metamorphism”), which bring their research routines close to those followed for metamorphic rocks [3]. In this way, modern methods of mineralogy, petrology and geochemistry are very useful for the study of archaeological ceramic materials [4]. Bricks in ancient buildings retain complex physico-chemical histories from the claystone geological formation to the finished product ready to be used in construction. From this point of view, a late history of changes, due to new pollution, different organic deposits and climatic variations, modifies the brick in dynamic equilibrium with its shifting environment. Thermogravimetric (TG) and Differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and porosimetric measurements of Byzantine and Medieval ceramics reveal interesting information on historical making processes and raw materials [5]. It is interesting to note that the central

dome of Hagia Sophia (Istanbul), built as early as 532 to 537 AD, was made entirely with brick and, after undergoing several restorations due to frequent earthquakes is still in use [6].

The nature, shape and size of different types of embedded grains and the brick matrix can be studied in a simple polarizing microscope allowing one to distinguish different raw materials, as follows: (i) sands of quartz, feldspars, mica, carbonate and accessory minerals (amphibole, pyroxene, garnet, sphene, etc.), (ii) fragments of plutonic, volcanic and metamorphic rocks, (iii) grog (ground brick-pottery added to clay) and (iv) matrix (colour, grain-size, texture). SEM provides high-quality imaging facilities together with semi-quantitative elemental analysis using energy-dispersive X-ray spectrometers (EDS), which have a wide range of applications in archaeological problems [7]. Data on the vitrification grade of ancient ceramics and their corresponding firing temperatures obtained by SEM examination are valuable for distinguishing between different traditions in ceramic technology in antiquity [8]. Electron probe microanalysis (EM), which combines electron microscopy with spot chemical analysis using mineral standards and wavelength comparison, leads in some cases to the precise identification of tiny mineral grains contained in the brick matrix and can be applied to determine their provenance [9]. As mentioned above, XRD and DTA are widely applied to the study of mineral phases and chemical compounds in ceramic materials [5,10]. Mössbauer spectroscopy is a very suitable technique for the study of iron phases in a wide range of samples and complex systems. It is particularly useful in the study of ceramic materials because the qualitative and quantitative analysis of iron compounds provides information related with colour, firing technique and fabrication technology of the ceramic [11-13]. In the study of ceramic materials, arrangements of complementary physicochemical methods provide more reliable results of archaeological significance than a single technique [4].

The aim of this study is to determine chemical and mineralogical composition, texture, structure and physical properties of bricks belonging to ancient buildings of Toledo City. The study was focused to select appropriate brick characterization routines to be applied in the restoration of historical buildings. This can constitute a good background to propose the use of: (i) rejected

ancient bricks, (ii) new special bricks made with claystone from the historical quarries, (iii) new material recipes based in the available commercial clays and additives. Data on alterations of brick surfaces could also be used as an indicator of paleo-climatic and pollution histories along the centuries. Thus, we present here a characterization study of ancient bricks of Toledo City by means of several techniques (Optical microscopy, SEM/EDS, EM, DTA, XRD and Mössbauer spectroscopy), as well as the determination of brick physical properties.

2. Materials and Methods

Brick samples were collected during refurbishment works from historical buildings in Toledo city centre (Spain). They were taken from a medieval brick wall in the Alcazar of Toledo (XII-XIIIth centuries) and from houses (XIII-XIVth centuries) of the Corralillo de San Miguel and named AL2 and COR, respectively. Both are representative samples of two ancient brick types: (i) AL2, apparently poorly baked with a pale reddish matrix and many fine detrital grains, and (ii) COR, displaying a creamy-coloured fine textured matrix with grog and melting vitreous-flows, suggesting a highly baked sample. In addition, several aliquots were prepared by re-firing brick samples at 700°, 800°, 900° and 1000° C for four hours. Analyses by XRD and DTA of neo-formed and remaining mineral phases after re-firings can be used to estimate the original firing temperature. Finally, to determine the geological origin of the brick raw materials, tiny mineral grains were extracted from the brick matrix after crushing with a hammer mill and screening with a sieve of 0.5 mm mesh size. Some minerals grains were also taken from the migmatite rock of the Toledo basement. The extracted grains were later classified under the optical microscope and next analysed and identified under the electron microprobe.

Thin-section examination under an optical polarising microscope was performed with a transmission light petrographic microscope (Nikon Eclipse C 600 POL) equipped with an automatic photographic system and a digital camera (Nikon Coolpix 950). The chemical compositions of mineral grains were determined by EM (Jeol Superprobe JXA-8900M), bulk and channel-selected (TAP, PETJ, LIF, PETH) X-ray spectra search and identification routines.

The standards used were natural and synthetic crystals from the collection of the "Centro de Microscopía y Citometría", Complutense University, Madrid. Textures, morphology and alteration products in clay bricks were also studied by SEM. For this technique, brick surfaces were coated with gold (20 nm) in a Bio-Rad SC515 sputter coating unit. General SEM observations were carried out in a Philips XL20 SEM at accelerating voltages of 20-30 kV. EDS were obtained using a Philips EDAX PV9900 with a light element detector, type ECON.

The brick mineralogy was determined by XRD using a Phillips PW-1710 powder diffractometer with CuK α radiation. Patterns were obtained by step scanning from 3° to 75° 2 θ with a count for 0.5 s per step, exploration speed of 7° minute⁻¹ and 40 kV and 40 mA in the X-ray tube. Differential thermal analyses (DTA) were recorded in atmospheric air, with a thermal analyser (Setaram, Labsys CS 32-CS 332 Controller). The heating was programmed with a first heating ramp from ambient to 80°C, with a heating rate of 20k minute⁻¹; a second heating ramp at 10k minute⁻¹ up to 1000°C, and an isothermal hold during 5 minutes at this last temperature. Samples were packed each time in alumina crucibles. The reference material was an empty alumina crucible.

⁵⁷Fe-Mössbauer spectra were recorded at room temperature in transmission mode with a conventional constant-acceleration spectrometer equipped with a ⁵⁷Co (Rh) source. Absorbers were prepared from powdered sample with a thickness of 100±10 mg cm⁻² using a PMM compression holder. The spectra were computer-fitted to a sum of Lorentzian lines by applying the constraints of equal line-width and area for the two peaks of each doublet, and equal line-width and areas in the ratio 3:2:1:1:2:3 for the six peaks of sextets. Isomer shifts (δ) were referred to the centroid of the spectrum of α -Fe at room temperature. The relative concentration of the different Fe species was calculated from the spectral area ratio assuming that the *f* factor (probability of Mössbauer effect) is the same in all the implicated species.

The study of physical properties was done according to quality standards tests UNE-EN. The determination of density was realised according to the standard UNE-EN 772-3:1999. Standards UNE 67027:1984 and 67031:1985-1986 were used in water absorption and suction tests,

respectively. Strength compression measurement was realized according to the standard UNE 67026 / 1M:1995 EX, using an Ibertest 1500 press. The velocity of charge was 8.5 kNs⁻¹. Finally, the porosity was determined by mercury intrusion porosimetry, using a Micromeritics Autopore III. S.9400.

3. Results and Discussion

Transparent slices of both types of bricks, under the polarizing microscope display coloured microcrystalline matrices and detrital grains of (i) biaxial quartz with anomalous extinction explicated from the surrounding migmatite rocks that have suffered huge geological stress, (ii) alkali feldspars with different sequences of exsolution perthites corroded with illite patinas, (iii) zoned plagioclase feldspars with polysynthetic twinning, (iv) strongly pleochroic brown biotite with zircon halos and chloritized borders of polarizing green colour. The distribution, composition, colour, size and shape of the grains are useful to compare pieces and speculate on origins of the raw material and firing temperature. Examining the claystone matrix, darker colours are linked with a more vitreous matrix and high firing temperature, while a light brownish colour indicates low firing temperatures. The sample AL2 shows isometric dark garnets with fissures filled by iron oxides. The clayed matrix of pale brown colour display grains of primary calcite, dolomite and biotite and secondary calcite in fissures (Fig. 1a). Under the crossed polarizing lens and larger magnification of the microscope (400x), it is also possible to observe tiny crystals of muscovite with bright colours.

The sample COR has a darker matrix and some glassy areas of magnesium and calcium aluminosilicates (diopside, gehlenite and melilite) in the boundaries of quartz, feldspars and phyllo-silicates. In principle, these findings can be associated to the use of higher firing temperatures in COR than in AL2 bricks. We will come to these results later.

Electron microprobe analyses of tiny grains (from 500 to 900 μm) taken from bricks, display the following empirical formulae: (i) almandine-garnet (Fe_{2.1}Mg_{0.62}Mn_{0.15}Ca_{0.08})Al₂(SiO₄)₃, (ii) pseudorutile Fe_{1.89}Ti_{2.98}O₉, (iii) calcite-dolomite Ca_{1.02}Mg_{0.05}(CO₃)₂, for AL2 sample, and (iv) alkali feldspar (K_{0.82},Na_{0.18})AlSi_{2.99}O₈, (v) quartz SiO₂ (vi) albite-anortite Na_{0.34}AlSi₃O₈ - Ca_{0.39}Al₂Si₂O₈

which corresponds with a labradorite plagioclase, for both samples. Theoretically, garnet phases could be helpful here in establishing linkages among bricks and raw materials, because they are metamorphic minerals formed at high temperature-pressure conditions resisting brick baking without undergoing mineral transformation, and Toledo surrounding regional rocks are migmatite with garnets. The garnets of AL2 sample can belong to detrital sands coming from the Toledo migmatite rocks, i.e., an intimate mixture of igneous material of granitic composition and high-grade metamorphic rocks of veined appearance. This type of rocks composes the basement of Toledo City centre (Fig. 2). The weathering detritus from migmatite rocks could be removed slope down by the erosion of the Tagus River, flowing downstream to the west, and deposited in the riverside banks in which the ancient claystone raw material were quarried. Conversely, the lack of garnet in COR sample suggests a different raw material location, probably upstream, in the east of the Toledo migmatite basement, out of the influence of the river erosion (Fig. 2). A garnet from the migmatite rock was analyzed (Table 1) showing the following empirical formula: $(\text{Fe}_{2.7}\text{Mg}_{0.24}\text{Ca}_{0.06})\text{Al}_2(\text{SiO}_4)_3$. It displays a composition of almandine-garnet close to those of AL2 bricks. The difference in it is the non-existence of manganese and a higher value of iron content. The EM image in Fig. 1b shows one of the garnet inclusions found in AL2 bricks. Chemical compositions obtained by EM for several of these garnet inclusions of AL2 samples and for the garnet of migmatite rock are shown in Table 1. The composition of these garnets agrees with those from the pluton-migmatitic Complex of Toledo fitting in the region of catazone metapelites into the Almandine-Pyrope-Spessartine garnets plot of Villaseca C. and Barbero L. [14]. This study classifies garnets from metapelitic rocks of the Spanish Central Region. Some analyses by EM of calcite-dolomite granules in AL2 samples display 60 wt % CaO and 2 wt % MgO. It is known that calcite and dolomite phases play an important role during firing due to the development of neoformed phases such as gehlenite and diopside.

We have used the SEM technique mainly to study chemical, physical, and biological alterations in bricks. Samples poorly baked, as AL2, display large amounts of secondary calcite re-crystallized in the porous system. These alteration processes are not simple, e.g. Fig. (1c) displays a euhedral habit of scalenohedron calcite crystal with corrosion pits and a surrounding empty space which could be

attributed to dissolution mechanisms. Figure (1c) also displays carbonated deposits onto the mineral surfaces. Figure 1d shows pores with druse crystallizations of slabs and needles of calcite, with chaotic spatial orientation, which can be interpreted by different flowing directions during the crystallization. Sample AL2 also encloses mineral deposits of biological origin; e.g., Fig. (1e) shows manganese micro-nodules linked to a biological film. Different types of biological items, i.e., lichen and algae associations, diatomeas, fungi hyphae and fungi bed, spores, etc. have been observed in the brick samples. These biological deposits are important in the late neo-formation phases from pollution mechanisms. Manganese micro-nodules (Fig. 1e) could be formed in AL2 bricks either by the action of reducing agents on aqueous solutions rich in anthropogenic KMnO_4 , or by oxidation mechanisms linked to algae-lichen biofilm because Toledo waters have high concentrations of alga biomass and manganese [15]. Conversely, samples highly heated as COR type bricks have characteristic details such as bubbles in the glassy-matrix clusters, and a diluted boundary grain-matrix. In addition, COR samples also display chlorides and calcium sulphates (Fig. 1f). In the polluted urban atmosphere of Toledo, deterioration of Ca-containing bricks has been accelerated to a great extent over the last decades. The main atmospheric pollutant is sulphur dioxide, which is very reactive and corrosive. Sulphur dioxide reacts directly forming sulphuric acid in the presence of water and oxidising agents. This reaction is the key step in the formation of gypsum onto the brick surface [16]. Sulphuric acid attacks both, carbonates and Ca-rich high-temperature silicates such as gehlenite and Ca-feldspars, giving rise to gypsum crystals [17]. The small amounts of sodium chloride present in the COR sample are explained by leakage of domestic chlorinated waters dissolving sodium from feldspars.

In both types of Toledo brick samples, XRD patterns (Fig. 3) show the most abundant and firing resistant phases, as follows: α -quartz (ASTM card 5-490) and feldspars such as albite (ASTM 9-466), anorthite (ASTM 12-301) and microcline (ASTM 19-932). The diffractogram of the original sample of AL2 also shows peaks corresponding to the following mineral phases (i) calcite (ASTM 5-586), (ii) dolomite (ASTM 11-78) and (iii) illite $2M_1$ (ASTM 9-334) (Fig. 3a). As shown above, optical polarising microscopy (see Fig. 1a) and SEM examination (Fig. 1c,d) indicate both primary and secondary origin for the calcite contained in AL2. Thus, the association of primary

calcite, dolomite and illite phases points to a low firing temperature (calcite and dolomite decompose circa 750°C and 800°C, respectively, and the illite phase does above 900°C). In Fig. 3 can be observed how new mineral phases (gehlenite and diopside) are formed at the expense of calcite and dolomite above 800°C. Diffractograms of the original and re-baked COR samples (Fig. 3b) show gehlenite (ASTM 20-199) and diopside (ASTM 11-654) peaks corresponding to neo-formed phases during the original firing by a reaction between the silica melt and calcium-magnesium phases (probably calcite and dolomite) existing in the clay paste. Summarizing, the presence of gehlenite and diopside in the COR sample indicates a brick fired at a temperature above 900°C, whereas in AL2 the presence of illite and primary calcite and dolomite points to a poorly baked brick with a firing temperature below 800°C.

DTA of AL2 and COR samples and their corresponding re-baked samples are linked in Fig. 4. DTA curves of both AL2 and COR samples show endothermic peaks below 100°C as the result of absorption water losses. AL2 curves recorded from the original and the 700°C re-baked sample are practically identical and show the following features: (i) an endothermic peak at 450°C explained by the possible dehydroxylation of illite, (ii) endothermic peaks at 650°C, 851°C and 930°C due to decomposition of calcite-dolomite; (iii) exothermic peaks at 911°C and 981°C attributed to the formation of a new crystalline phase; (iv) a little endothermic peak circa 575°C attributed to the α - β quartz structural transition. Original, 700°C and 800°C curves of AL2 show also some small endothermic and exothermic peaks above 850°C linked to the destruction of illite and recrystallization of new phases in a complex fluid-gas process. Curves corresponding to AL2 samples re-baked at 800°C and 900°C exhibit a large endothermic peak circa 450°C, indicating losses of hydroxyl groups from the $\text{Ca}(\text{OH})_2$ formed by re-hydration of the CaO exposed to environmental humidity. This fast hydration of CaO shows how rapid chemical changes are when calcareous claystone is used for brick fabrication. Taken together these DTA data, an original firing temperature below 800°C can be proposed for AL2. In the COR sample, there are no appreciable differences between the original and the 700°, 800° and 900°C curves, whereas the 1000°C curve is clearly different (Fig. 4b). Original, 700°C, 800°C and 900°C curves show three endothermic peaks

at 300°, 575°, 785°-830°C and an exothermic peak at 860°C. Endothermic peaks at 300° and 575°C can be attributed to α and β cristobalite and quartz phase transitions, respectively. Endothermic peaks at 785°-800° are associated with the presence of calcium silicates and the exothermic peak at 860°C indicates the presence of diopside. This allows an estimate that the COR bricks were baked at a firing temperature between 900° and 1000°C.

Mössbauer spectra of both AL2 and COR samples show the typical pattern of an ancient ceramic: a main paramagnetic doublet in the central part of the spectrum and a magnetic component with rather broad lines (Fig. 5). In the COR spectrum this magnetic component appears to be composed of at least two sextets. Spectra were best fitted to a doublet (A) and a sextet (B) in AL2, and to a doublet (A) and two sextets (B and C) in the case of the COR spectrum. Table 2 gives the parameters and relative concentrations of the different species calculated from the fitted spectra. As can be seen, only Fe^{3+} species are present in the spectra indicating that samples were fired in an oxidizing atmosphere. The parameters of the doublet correspond to Fe^{3+} in an octahedral coordination and allow the doublet assignment either to substitutional Fe^{3+} in the clay mineral structure or to superparamagnetic ferric oxides [11,18]. Quadrupole splitting values of the doublet allow one also to infer a rough estimation of the firing temperatures as below and above 800°C for samples AL2 and COR, respectively [11,19]. From its hyperfine parameters (Table 2), sextet B can be identified as hematite ($\alpha\text{-Fe}_2\text{O}_3$) [20]. The low H value and line broadening of sextet B in the AL2 spectrum is attributable to the presence in this sample of substituted forms of hematite (Al-substituted hematite, $\alpha\text{-(Fe}_{1-x}\text{Al}_x)_2\text{O}_3$, for example) [20]. The important magnetic relaxation exhibited by sextet C at room temperature (RT) indicates that the ferric oxides contributing to this sextet are finely divided in particles of small size ($< 100\text{\AA}$). Finally, in both samples the magnetic ratio (Mr) has RT values of *ca.* 0.20 (see Table 2). This Mr value is compatible with the use of calcareous claystone as the raw material in which chalk particles inhibit the hematite formation during the baking [11, 21].

The physical properties of ancient bricks of Toledo range from poorly-fired samples (AL2) up to highly-fired samples (COR), as follows: Water absorption (19.0% – 22.0%), Water suction (0.08%

– 0.18%), Density ($1.60 \text{ g/cm}^3 - 1.51 \text{ g/cm}^3$), Compression Strength ($334.73 \text{ daN/cm}^2 - 337.14 \text{ daN/cm}^2$), Total Porosity (32.46% - 43.12%) and Mean Average Pore ($0.13 \mu\text{m} - 0.61 \mu\text{m}$). The AL2 sample has less total porosity than sample COR. The high value of the total porosity and mean average pore size of the COR sample is explained by degasification of hydroxyl groups of phyllosilicates and by the effect of CO_2 formed during firing from carbonates. The presence of gehlenite and diopside in the COR sample indicates that a calcareous paste was used. Above 800°C , the fluxing action of the alkaline oxides, coupled with the CO_2 , seems to be responsible for the glass froth, and consequently, to the relationships between the final brick porosity and the amount of glass. The lower water absorption and suction values obtained for the poorly-fired AL2 brick in respect to the highly-fired COR brick could be attributed to both, low porosity and pore cementation by calcite in the AL2 sample. Surprisingly, both AL2 and COR samples have similar compression strength measurements. The mentioned cementation of pores in AL2 bricks could explain the high value obtained for its compression strength, anomalous in bricks fired at low temperatures. These suitable values of physical properties demonstrate that these ancient bricks were handcrafted with adequate raw materials and under the right conditions of temperature, kiln atmosphere, baking time, etc. It is critical to note that the carbonate content in the raw material of bricks is twofold: (i) minor amounts lead to further consolidation of the brick matrix by pore and fissure cementation, and (ii) carbonate overload produces coherence losses between phases and subsequent brick deterioration.

4. Conclusions

Accessory minerals such as almandine-garnet identified by EM in AL2 bricks let us infer that they were made with raw materials from quarries settled in the western part of the migmatite basement of Toledo City. However, the lack of garnets in COR bricks suggests that raw materials were collected from quarries located in the eastern surroundings of Toledo.

XRD and DTA studies of mineral phases present in bricks, before and after re-firing experiments, complemented by optical polarising microscopy and SEM to determine primary or

secondary minerals, indicate ancient firing temperatures of: (i) above 900°C for the COR sample (because it contains gehlenite and diopside), and (ii) below 800°C for the AL2 sample, as prove the illite and primary calcite / dolomite content and the mineralogical changes after re-firings.

Mössbauer results allow one to deduce that oxidizing firing conditions, pastes made from raw calcareous claystone, and firing temperatures above and below 800°C for COR and AL2 samples, respectively, were used in the fabrication of these bricks.

Paleo-climatic and pollution products and micro-organisms (lichen, algae, diatoms, fungi, spores), detected by SEM in brick surfaces, are indicators of the historical environmental conditions. Sulphates detected in COR bricks prove their urban atmosphere exposition, whereas manganese micro-nodules and abundant organic deposits in AL2 suggest underground environments.

The data obtained on mineral composition, original firing temperature and physical properties of ancient bricks are an essential background to elaborate new specific bricks for restoration purposes.

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Figure Captions

Figure 1. (a) Thin-section under an optical polarising microscope of the AL2 brick sample, showing rounded primary calcite grains [Cal_p] and a fissure filled with secondary calcite [Cal_s]; (b) Electron Microprobe image of a pyrope-garnet [Grt] taken from AL2 brick, the surrounding material is alkali feldspar [Fs]; (c) Rhomboedron of secondary calcite covered by late secondary calcite (SEM image); (d) Secondary calcite crystals in a pore of AL2 (SEM image); (e) Manganese micro-nodules growing under a bio-film onto the brick surface of AL2 (SEM image); (f) Gypsum crystals [Gp] onto the COR brick surface (SEM image). Abbreviations of minerals according to Kretz R. (1983) [22].

Figure 2. Geological setting of Toledo City surroundings.

Figure 3. X-ray diffraction patterns of original and re-fired samples corresponding to ancient bricks of Toledo: (a) AL2 and (b) COR.

Figure 4. Differential thermal analyses of original and re-fired samples: (a) AL2 and (b) COR bricks. Note as the poorly-fired AL2 sample shows an endothermic peak circa 850°C due to CaCO₃ decomposition, whereas the highly-baked COR brick displays a double endothermic peak at 785° - 800°C linked with the presence of calcium aluminosilicates.

Figure 5. Mössbauer spectra recorded at room temperature from AL2 (a) and COR (b) samples. The computer fits are shown as solid lines and the subspectra obtained are labelled as A, B, and C (see Table 2).

TABLES

Table 1. Electron microprobe analyses (wt %) of garnet inclusions taken from AL2 bricks (Grt-48, Grt-73, Grt-80) and from the migmatite rock of Toledo basement (Grt-MigTo)

Table 2. RT Mössbauer parameters (δ = Isomer shift, relative to α -Fe; Δ = Quadrupole splitting; 2ε = Quadrupole shift; Γ = full linewidth at half maximum; H = Magnetic hyperfine field; I_{rel} = Relative spectral area; Mr = Magnetic to Total spectral area ratio, I_B+I_C/I_{tot} . Numbers in parentheses give the uncertainty in the last digit).

Table 1						
	Si	Al	Fe	Mn	Mg	Ca
Grt-48	38.0	21.3	32.8	0.9	5.0	0.5
Grt-73	38.1	21.5	32.4	0.9	5.1	0.5
Grt-80	38.1	21.3	32.5	0.9	5.1	0.5
Grt-MigTo	33.1	17.8	42.3	-	3.9	0.9

Table 2		
	AL2	COR
<u>Doublet A</u>		
δ (mm s ⁻¹)	0.36 (1)	0.36 (1)
Δ (mm s ⁻¹)	1.14 (1)	0.96 (1)
Γ (mm s ⁻¹)	0.69 (6)	0.64 (1)
I_{rel} (%)	78.1 (5)	79.3 (9)
<u>Sextet B</u>		
δ (mm s ⁻¹)	0.37 (1)	0.41 (1)
2ε (mm s ⁻¹)	-0.22 (3)	-0.30 (3)
Γ (mm s ⁻¹)	0.69 (5)	0.41 (5)
H (T)	49.9 (1)	50.8 (1)
I_{rel} (%)	21.9 (9)	5.3 (7)
<u>Sextet C</u>		
δ (mm s ⁻¹)	-	0.28 (5)
2ε (mm s ⁻¹)	-	0.12 (8)
Γ (mm s ⁻¹)	-	1.8 (2)
H (T)	-	42.5 (4)
I_{rel} (%)	-	15 (2)
<i>Mr</i>	0.22	0.21

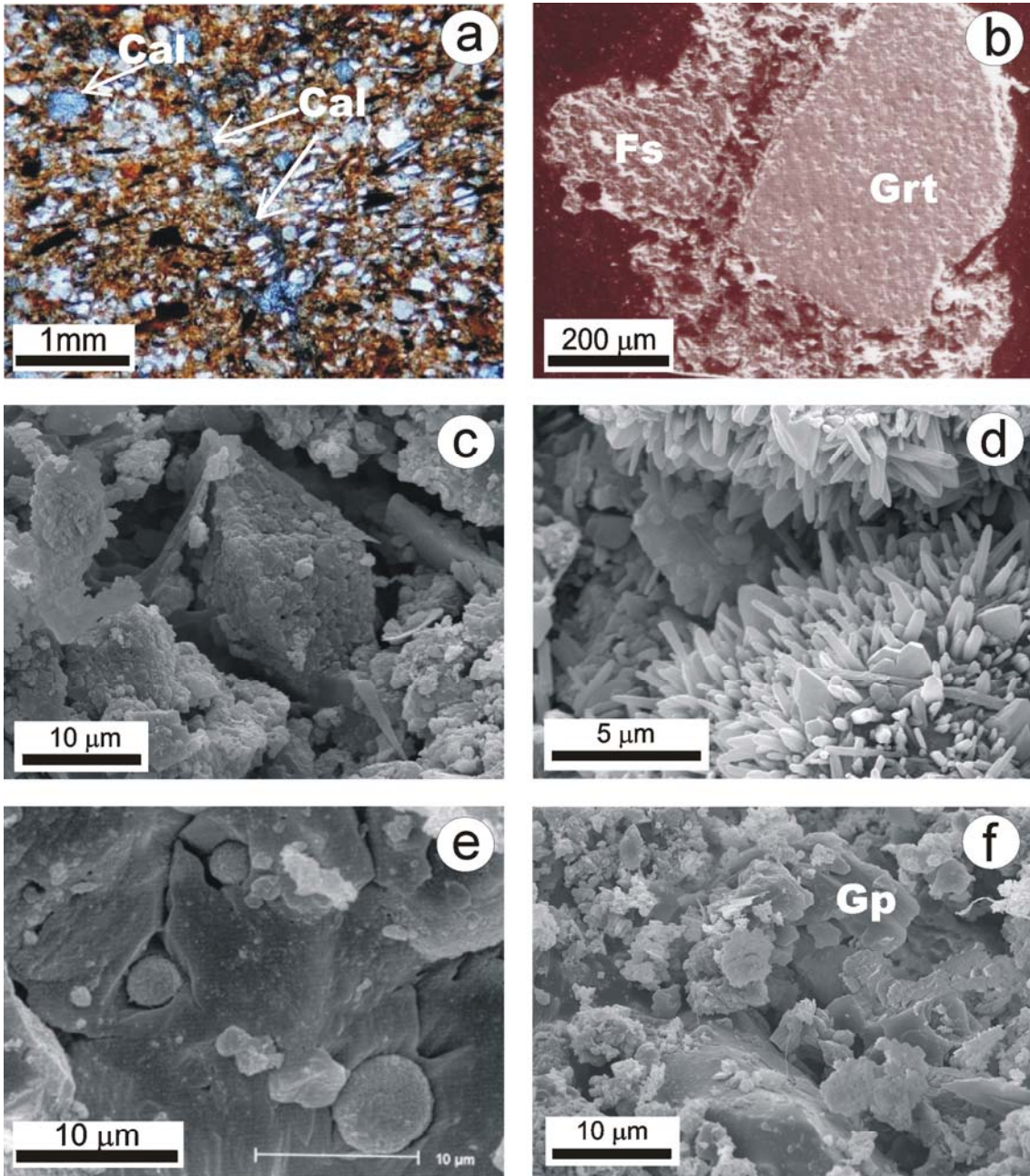


Figure 1
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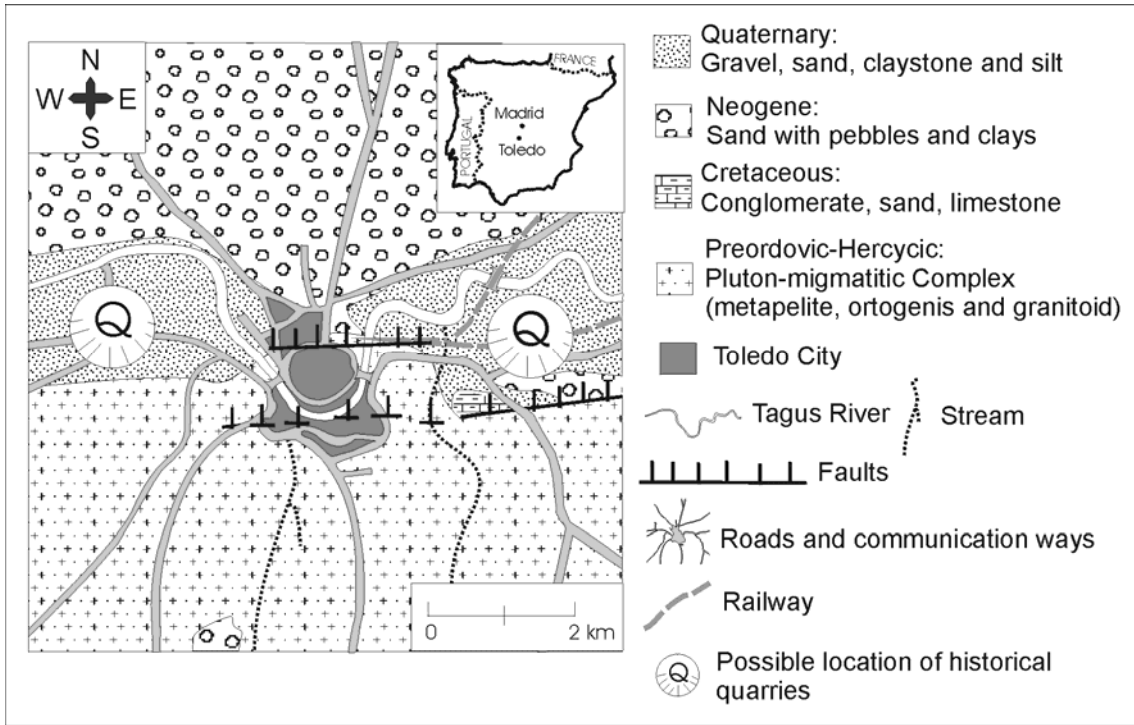


Figure 2
Lopez-Arce et al.

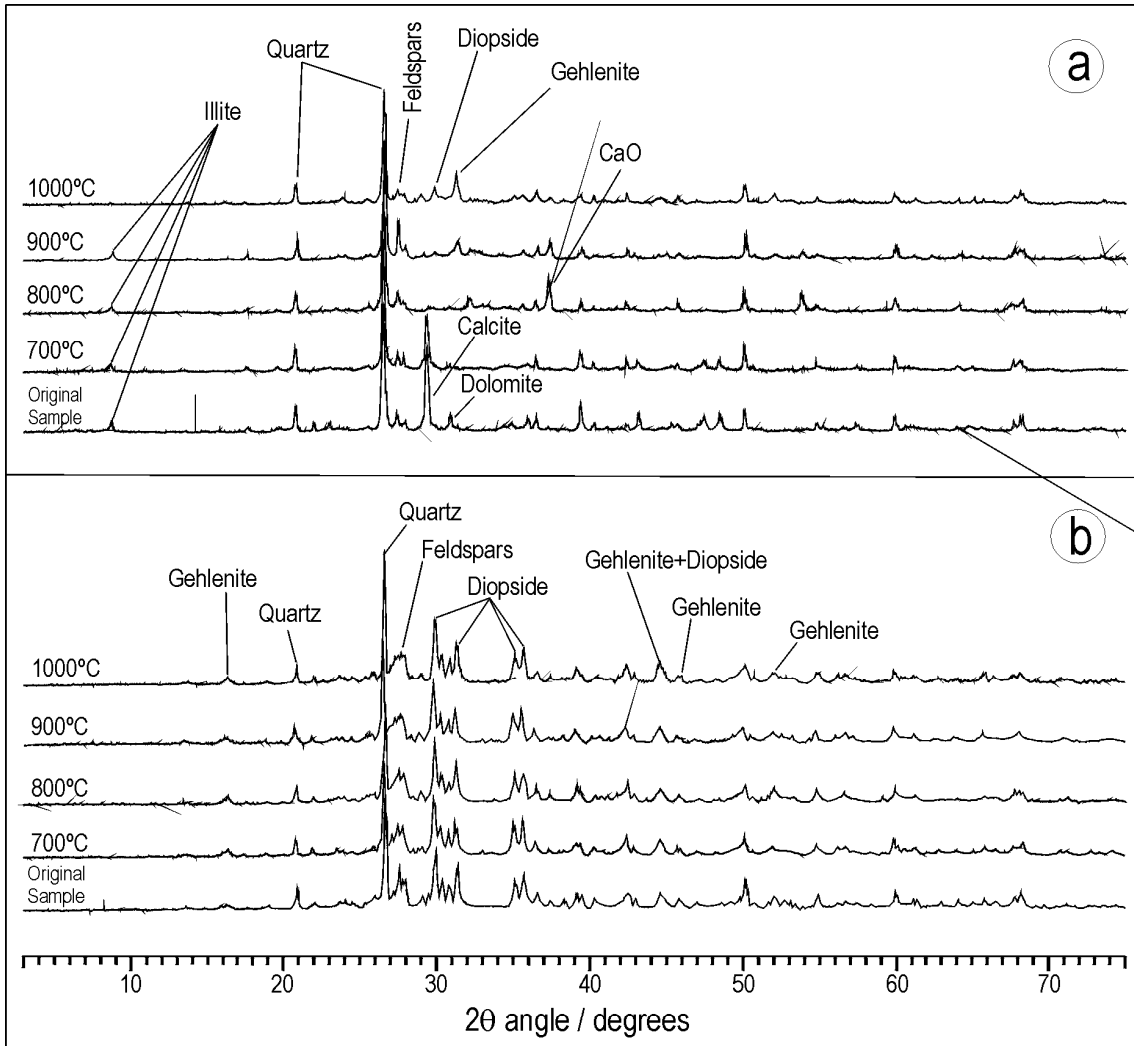


Figure 3
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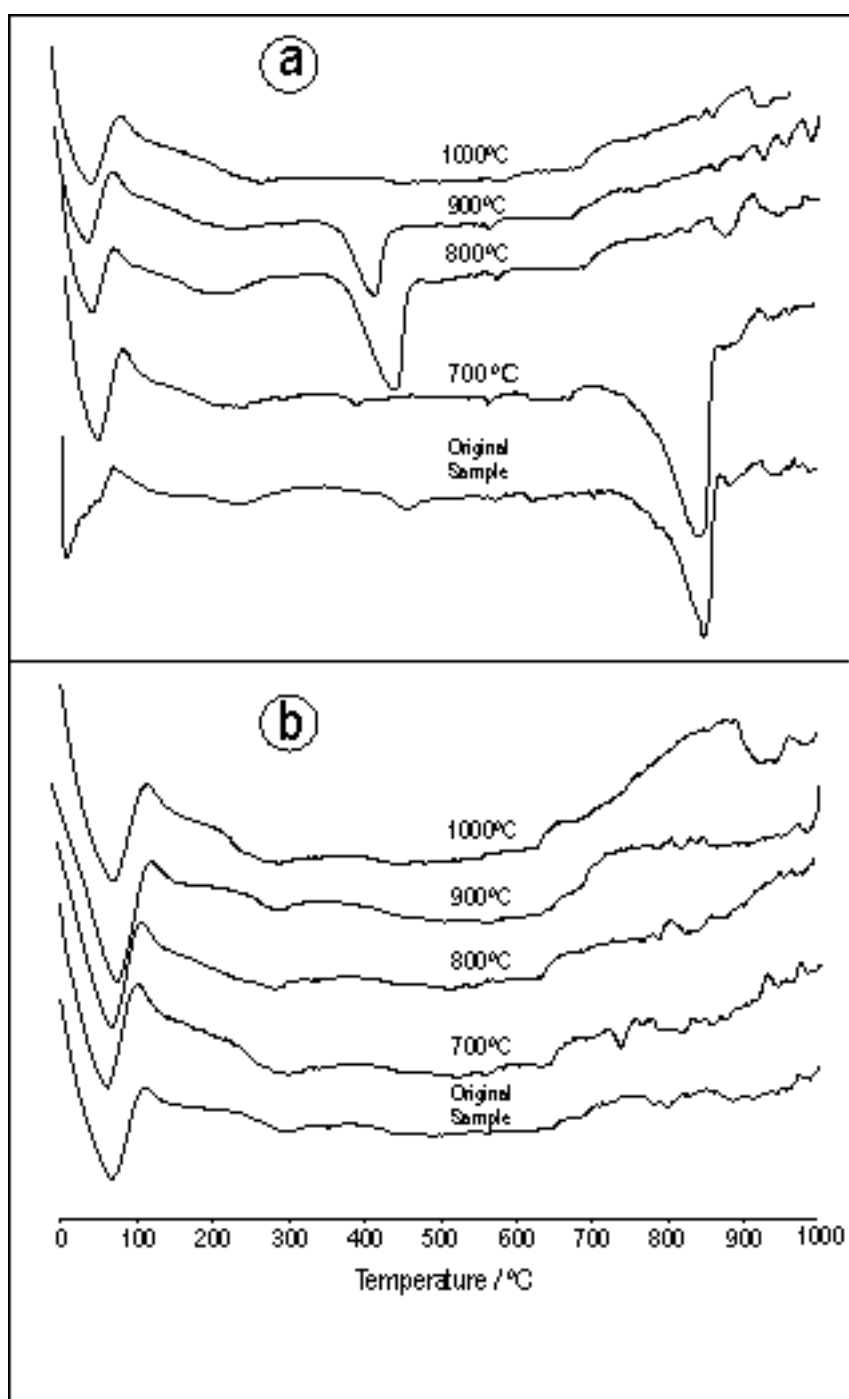


Figure 4
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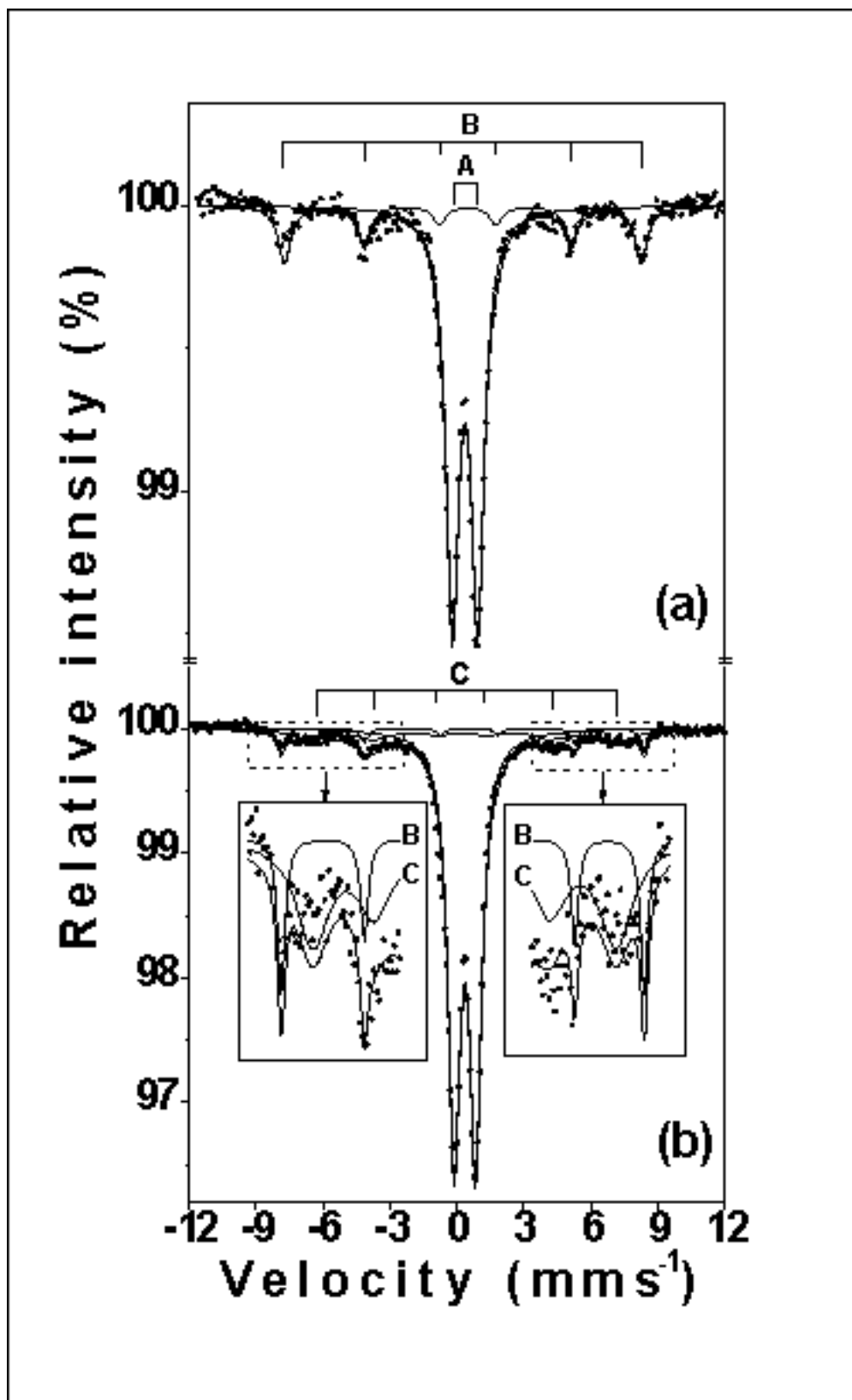


Figure 5
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