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Evaluation of ATR-FTIR spectroscopy for distinguishing anthropogenic and geogenic calcite.

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Abstract. Infrared spectroscopy allows to reliably distinguish between calcites formed by different processes, e.g. geogenic and anthropogenic calcite. This approach can be used for rapid sample analysis in the radiocarbon dating of mortars. The datable component is represented by anthropogenic calcite, that results from the reaction of calcium hydroxide with the atmospheric CO₂ during the hardening of the material. However, different possible sources of contamination can alter the true radiocarbon concentration and can thus make the mortar appearing either older or younger. The preventive identification of the origin of calcite present in the sample allows to measure only anthropogenic calcite, reducing the time and cost of Accelerator Mass Spectrometer (AMS) measurements. Many papers are present in the literature discussing the use of Fourier transform infrared spectrometry (FTIR) with the KBr pellet method, to distinguish the origin of calcite. In this paper, the use of attenuated total reflectance mode (ATR-FTIR) is evaluated since it may present valuable advantages such as non-destructivity, in the perspective of sample reuse for dating.

1. Introduction

The origin of different calcite fractions in archaeological mortars has been determined by using Fourier transform infrared spectroscopy (FTIR) technique in transmission mode on KBr pellet, to characterize the extent of atomic order/disorder in the calcite crystal structure [1-3]. Indeed, the ν_2/ν_4 ratio of calcite, corresponding respectively to the out-of-plane bending (874 cm^{-1}) and to the in-plane bending (713 cm^{-1}) vibrations of the carbonate ions, can be used to differentiate between anthropogenic calcite (e.g. in plaster or mortars), where the crystal structure is extremely disordered, from geogenic calcite (e.g. in limestone), which has an ordered structure. This method lends itself to the selection of the most suitable mortar portion for dating with the radiocarbon method [4-5]. The identification of the mineralogical phases, the chemical-physical characterization of the sample, and the assessment of whether a “datable fraction” can be separated by chemical or physical means are the main steps for the preparation of sample for dating. Once the material has been selected, it is necessary to carry out a further characterization, to verify the quality of the binder-aggregate separation. Therefore, assuming we have small quantities of sample, it is necessary to select a non-destructive spectroscopic technique,



as FTIR in attenuated total reflectance mode (ATR) to preserve the material for further analyses. Samples of geological and anthropogenic calcite were selected to evaluate whether the ATR-FTIR mode could lead to the same results as the FTIR technique with KBr pellet.

2. Materials and methods

Geogenic samples were collected in Italian quarries: limestones and white marbles from Apuan Alps (Tuscany, Italy); limestones and marly limestones from Monte Morello formation (A and L) (Tuscany, Italy), Pietra di Lecce, Pietra di Vicenza, Travertine from Rapolano.

Different kinds of anthropogenic calcite samples were analysed:

- 1- four different types of fresh plasters obtained by calcination and slaking of the limestone samples, mixed with silicate sands and cured for 5 years (LS01-04);
- 2- modern binder samples factory-made (Bioedilizia): Bio-lime, white natural hydraulic lime (WHL) and hazelnut natural hydraulic lime (HHL);
- 3- medieval historical mortars taken from Giotto's Bell Tower (Florence, Italy), roman historical plasters from archaeological sites in Ostia Antica (Italy) (OS), Utica (Tunisia) (UT09, UT10, UT11), etruscan plaster from Norchia (Italy) (TCR01-TCR02). For Giotto's Bell Tower samples, bulk and lumps were analysed (G lump 1, G lump 2, G lump 3, G bulk 1, G bulk 2).

Fourier transform infrared spectroscopy (FTIR) was employed to identify calcite derived by mortar/plaster or stone, analysing samples with the KBr pellet method in transmission mode (hereinafter referred to as KBr) and a diamond ATR system (ATR). The acquisition was carried out in the spectral range between 4000 and 400 cm^{-1} , with a resolution of 4 cm^{-1} for 24 scans. To compare the results obtained in transmission and ATR modes, the spectra were processed using OPUS 7.2 software and Spectragryph v 1.2.15. Furthermore, ATR spectra were corrected with the dedicated function of the OPUS software.

Figure 1 shows a typical FTIR spectrum of calcite. The values of ν_2 and ν_4 are collected by the height of the ν_2 peak and by the height of the ν_4 peak. The baselines were drawn between the closest minima on either side of the measured peak (Figure 1), following the methods by Chu et al. [1] and Regev et al. [2]. These spectra represent the same sample analysed by KBr pellets (spectrum a) and ATR-FTIR mode (spectrum b).

For each sample, a few milligrams of sample were homogenized and powdered in an agate mortar with a pestle. About 1 mg was used for the ATR analysis, while another 1 mg was mixed with 80 mg of KBr and pressed into a pellet using a manual hydraulic press. Each sample was analysed through constant aliquots of the sample, by 3 pellet samples and 3 powder samples. The reproducibility of the ν_2 and ν_4 values was determined by analysing each sample 3 times.

The ν_2 and ν_4 heights were normalized to a ν_3 height of 1000, corresponding to 1.0 absorbance unit, following the method of processing of data by Regev et al [2]. Then, the ratios ν_2/ν_4 were calculated, to process the data as proposed by Chu et al. [1].

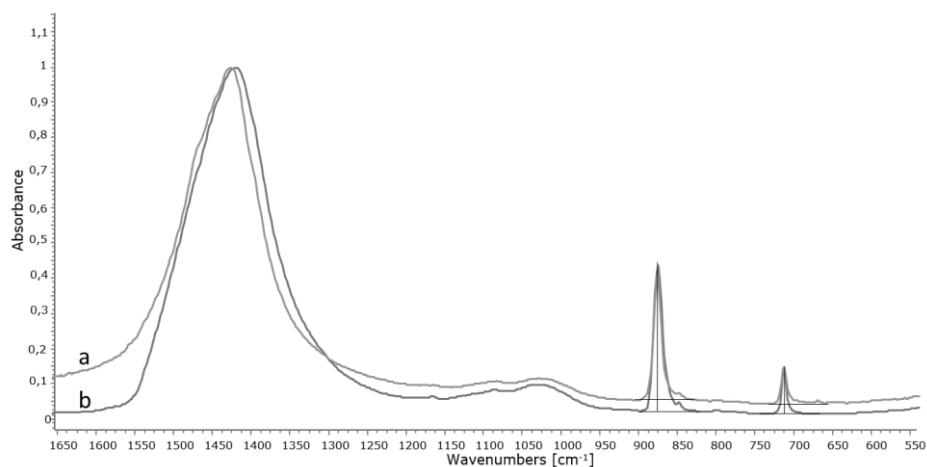


Figure 1. Comparison of infrared spectra of Alberese Limestone A: in a) FTIR spectrum in transmission mode, on KBr pellet; and in b) ATR-FTIR spectrum.

The peaks at 1420, 874 and 713 cm^{-1} correspond to the ν_3 , ν_2 and ν_4 absorption bands of calcite, respectively. The ν_2 and ν_4 peak heights were normalized relative to the height of the ν_3 peak. The spectra are not baseline corrected. The spectrum b was ATR-corrected.

3. Characterization of ancient mortars/plasters and anthropogenic calcite selection

A preliminary minero- petrographic characterization was carried out for each ancient mortar/plaster, in order to investigate the sample layering, to characterize binder, aggregate, lumps and possible additives and to address sampling for FTIR analyses [6].

The medieval historical mortars taken from Giotto's Bell Tower (Florence, Italy) consist of a natural hydraulic lime binder, obtained from a marly limestone, known in the Florentine area as Pietra Alberese (Monte Morello Formation). The aggregate was obtained from the bed of the Arno River, its composition is mainly silicatic, free of organic substances [7]. Sieved bulk and lumps of binder portions were selected for spectroscopic investigation on calcite.

The sample coming from Ostia Antica (Italy) archaeological site belong to a ceiling decoration, made of three layers: a first painted layer, a second one made of calcic lime added with travertine and calcite crystals, a third layer obtained mixing lime with fragments of volcanic rocks, pyroxenes and few carbonate rocks [8]. This last layer (Figure 2a) was selected for FTIR analyses.

The plasters coming from Utica (Tunisia) archaeological site revealed, under the painted layer, a layering made of lime added with sub-rounded grains of quartz (*unpublished data*) (Figure 2b).

The Etruscan plaster from Norchia (Italy) was made by mixing lime binder with red pozzolanic rock fragments (*unpublished data*).

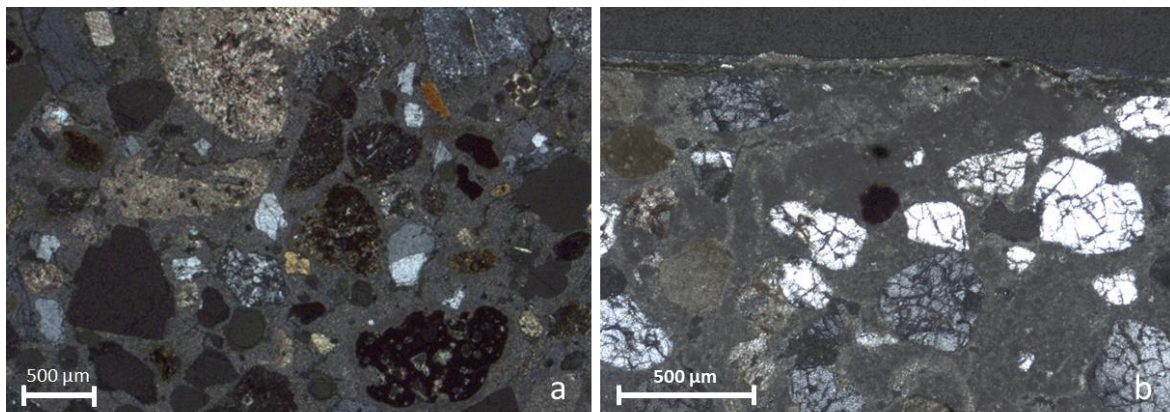


Figure 2. Microphotograph of thin section under polarized microscope of the selected plaster layer (crossed nicols; bar 500 μm) for ATR FTIR analyses: a) Ostia Antica sample; b) Utica sample.

4. Results and discussion

For each sample, Table 1 reports the average ratio v_2/v_4 in ATR and KBr mode. Limestone samples produced v_2/v_4 ratios around 3, ranging from 2.14 to 3.42, in KBr mode and from 2.79 to 3.63 in ATR, which is consistent with reported literature results for geogenic calcite. Plasters prepared from lime, produced in laboratory (LS01-04), presented a v_2/v_4 ratio ranging from 5.52 to 8.47 (KBr). Instead, standard mortar samples (Bio-lime, WHL, HHL) showed v_2/v_4 ratios from 5.29 to 6.91 (KBr) and 5.43 to 6.78 (ATR). The mortars/plasters from the case studies generally have v_2/v_4 ratios ranging from 5 to 7. Indeed, with exception of the Giotto's Bell Tower samples, the mortar samples were analysed with both methods, producing v_2/v_4 ratio from 4.96 to 6.36 (KBr) and from 5.62 to 7.09 (ATR).

Figure 3 shows the plots of the v_2 vs. v_4 peak height trend lines of geogenic and anthropogenic calcite obtained in transmission (Figure 3a) and ATR mode (Figure 3b). The different trend lines in Figure 3 show that there is a systematic difference in the v_2 vs. v_4 peak heights for calcites that were formed in different ways. The blue shallowest slope corresponds to sample composed by geogenic calcite, which is known to have high atomic order over macroscopic length scales, while the orange steepest slope corresponds to a lime plaster samples. Such different trend is identified using both techniques ATR and Transmission. The data from unknown samples can then be located on the master plot and preliminary conclusions can be drawn about the origin of their formation. The possibility of identifying the origins of calcite using the ATR technique is highly advantageous for the research field of mortar dating, since it is not destructive for the powdered sample which can be recovered and reused for dating, if the sample consists of anthropogenic calcite.

Table 1. Comparison of average v_2/v_4 ratio of archaeological mortar/plaster and geological samples investigated in transmission (KBr) and ATR mode.

Samples	v_2/v_4 ratio	
	KBr	ATR
White Marble	2.14	2.79
Limestone	3.42	3.63
Alberese Limestone A	2.92	3.55
Alberese Limestone L	2.75	3.13
Pietra di Vicenza	3.13	3.43
Pietra di Lecce	2.81	3.31
Travertine	2.43	2.96
LS01	8.04	-
LS02	7.25	-

LS03	8.47	-
LS04	5.52	-
Bio-lime	5.29	5.43
WHL	6.91	6.78
HHL	6.14	6.42
G lump 1	-	6.28
G lump 2	-	7.09
G lump 3	-	5.99
G bulk 1	-	6.38
G bulk 2	-	5.88
OS	6.36	6.89
TCR 01	4.96	7.09
TCR 02	5.93	6.40
UT 09	4.98	5.62
UT 10	6.03	5.62
UT 11	5.06	5.77

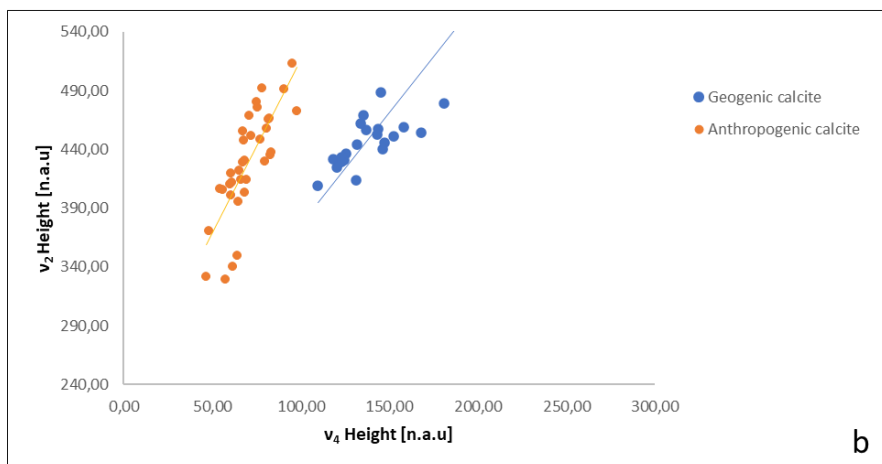
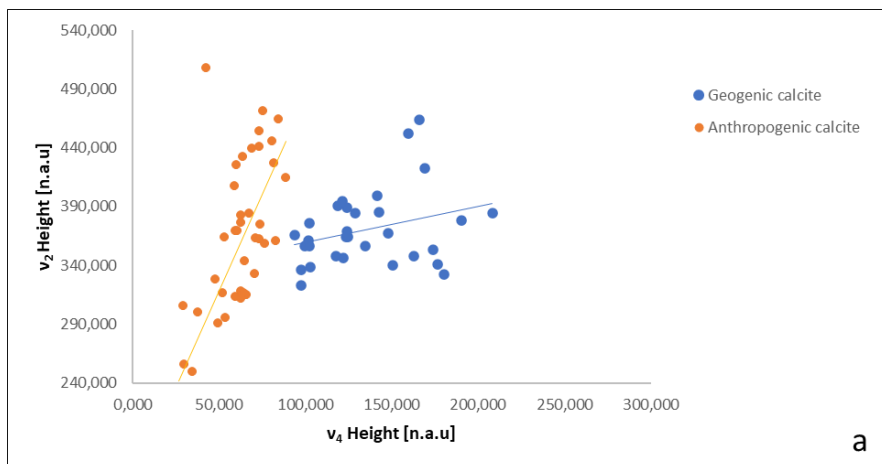


Figure 3. Plot of the v_2 vs. v_4 peak heights of geogenic and anthropogenic calcite and normalized to the corresponding v_3 peak height. In a) Plot of v_2 and v_4 obtained in transmission mode in KBr pellet; in b) Plot of v_2 and v_4 obtained in ATR mode, after ATR-correction spectrum. The blue shallowest slope corresponds to sample composed by geogenic calcite, which is known to have high atomic order over macroscopic length scales, while the orange steepest slope corresponds to a lime plaster samples.

5. Conclusion

FTIR spectroscopy is an efficient, rapid, and effective tool to distinguish between calcites formed by different processes. This method can be applied in ATR-FTIR mode, enabling the distinction of anthropogenic and geogenic calcite, as well as a non-destructive further analysis of samples to be dated with radiocarbon method.

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