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The presence of vaterite in bonding mortars of marble inlays from Florence Cathedral

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DURING the study of some decay processes in marble covering the façade of the Florence Cathedral (1870–1887), vaterite was found as the principal component of some bonding mortars of inlay decorations.

Vaterite is one of the three polymorphous phases of $CaCO_3$ and crystallizes in the hexagonal system, dihexagonal bipyramidal class (Kamhi, 1963; Sato and Matsuda, 1969): it is unstable under normal environmental conditions (Deer *et al.*, 1964). Nevertheless, during recent years, the presence of vaterite has been confirmed in different situations: i.e. gastropod tissues, gallstones, urinary calculi, drilling muds (Friedman and Schultz, 1994), and Portland cement (Cole and Kroone, 1959).

The bonding mortars were studied with the purpose of identifying the cause of alteration of the marble inlays that showed serious decay. They were analysed with X-ray diffractometry (XRD), thin section optical microscopy, and infrared spectrophotometry (FT-IR).

Five samples, placed in two groups according to their colours (grey and light ochre), were analysed. Both were composed mainly of a hydraulic binder: the grey bonding mortar showed an equal amount of calcite and hydrated calcium silico-aluminates, while the light ochre one consisted of vaterite with a small amount of aragonite, calcite and hydrated calcium silico-aluminates.

The FT-IR spectra of both groups, recorded from a KBr pellet, are reported in Fig. 1. Despite literature claims (Weir and Lippincott, 1961; Sato and Matsuda, 1969; Ducloux *et al.*, 1987; Andersen and Brecevic, 1991) vaterite shows only one absorption at 1476 cm^{-1} due to the CO_3^{2-} asymmetrical stretching (ν_3), while the other absorptions at 876 and 850 cm^{-1} (out of plane bending, ν_2), and at 746 cm^{-1} (in plane bending, ν_4) agree with the data reported in the literature mentioned above. In this case, the ν_1 vibration around 1100 cm^{-1} was not detectable because of the presence of hydrated calcium silico-aluminates.

The FT-IR spectra of vaterite synthesised following Davies *et al.* (1978) are more complex than those of the Cathedral mortars. The XRD analysis, however, shows only vaterite even if diffraction patterns appear with a too low intensity in respect to a pattern of a completely crystalline compound. In order to explain the differences in the FT-IR spectra and in the diffraction patterns between the synthetic and natural product, more syntheses of vaterite were made changing some parameters (i.e. concentration of reagents and the rate of addition) with respect to Davies *et al.* (1978). The results, still

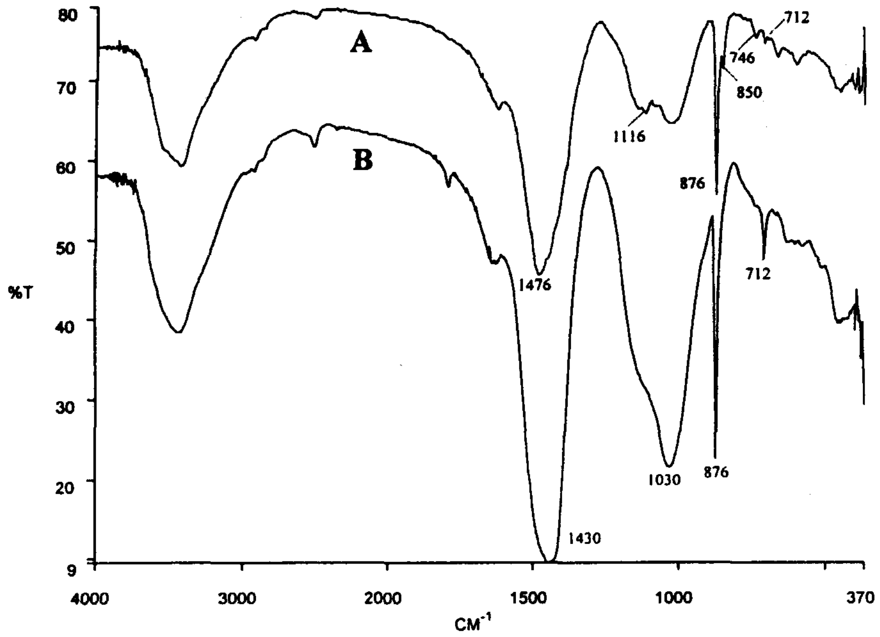

FIG. 1. FT-IR spectra of light ochre (A) and grey (B) bonding mortar from the façade of the Florence Cathedral.

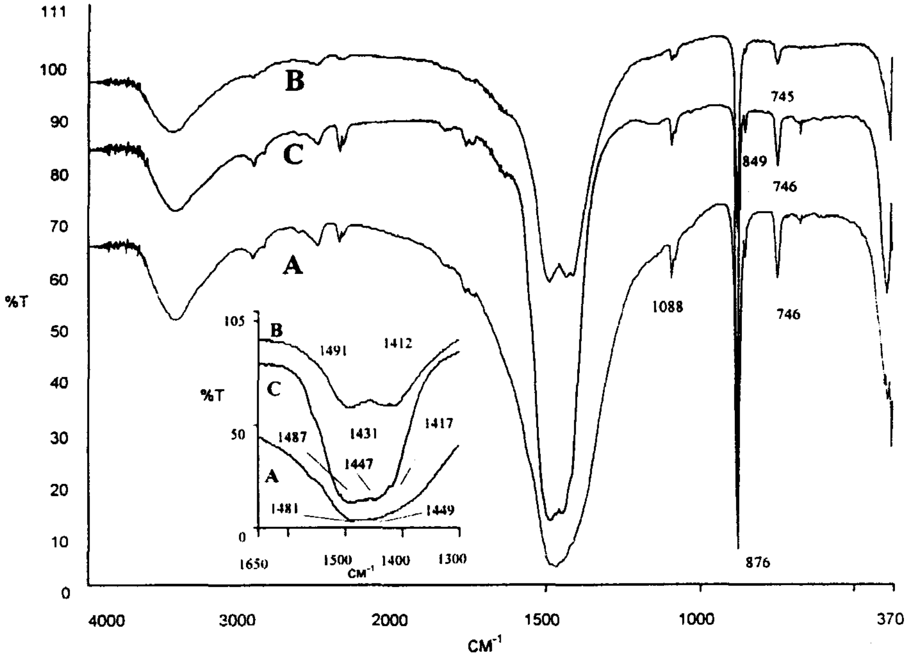

FIG. 2. FT-IR spectra of synthetic vaterite: (A) 0.2 M calcium nitrate was very slowly added to 0.2 M sodium carbonate containing 0.025 M sodium sulphate (Davies *et al.*, 1978); (B) 0.2 M calcium nitrate was quickly added to 0.2 M sodium carbonate containing 0.025 M sodium sulphate: precipitate formed immediately; C) precipitate formed in the mother waters of the previous synthesis (B).

being obtained, indicate the precipitation of vaterite and amorphous calcium carbonate at the same time. The latter has the main absorption (v_3) at 1492 cm^{-1}, in good agreement with Andersen and Brecevic (1991). The spectra, however, show other absorptions in the 1410–1470 cm^{-1} interval, where intensity and frequencies are strictly related to the synthesis followed (Fig. 2).

Further studies on this topic, and particularly, about the conditions of crystallization of vaterite in hydraulic mortars are in progress.

References

Andersen, F.A. and Brecevic, L. (1991) Infrared spectra of amorphous and crystalline calcium carbonate. *Acta Chem. Scand.*, **45**, 1018–24.

Cole, V.F. and Kroone, B. (1959) Carbonate minerals in hydrated portland cement. *Nature, Brit. Assoc.*, **B.A.**, 57

Davies, P., Dollimore, D. and Heal, G.R. (1978) Polymorph transition kinetics by DTA. *J. Thermal Anal.*, **13**, 473–87.

Deer, V.A., Howie, R.A. and Zussman, J. (1964) *Rock-forming Minerals – V. 5, Non-silicates*. London, Longman, Green and Co Ltd, 372 pp.

Ducloux, J., Dupuis, T. and Laouina, A. (1987) Influence de gels mineraux et d'argiles sur la cristallogenese du carbonate de calcium a partir des solutions bicarbonatees. *Catena*, **14**, 553–60.

Friedman, G.M. and Schultz, D.J. (1994) Precipitation of vaterite ($CaCO_3$) during oil field drilling. *Mineral. Mag.*, **58**, 401–8.

Kamhi, S.R. (1963) On the structure of vaterite, $CaCO_3$. *Acta Crystallogr.*, **16**, 770–2.

Sato, M. and Matsuda, S. (1969) Structure of vaterite and infrared spectra. *Z. Kristallogr.*, **129**, 405–10.

Weir, C.E. and Lippincott, E.R. (1961) Infrared studies of aragonite, calcite, and vaterite type structures in the borates, carbonates, and nitrates. *J. Res. NBS – A Physics and Chemistry*, **65A**, 3, 173–83.

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Phosphatian coffinite with rare earth elements and Ce-rich françoisite-(Nd) from sandstone beneath a natural fission reactor at Bangombé, Gabon

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SPONTANEOUS fission reactions occurred in several uranium deposits in SE Gabon approximately two billion years ago. The reactor zones, between 10 to 50 cm thick, are found in Proterozoic sandstones and consist of high-grade uranium ore mantled by illite and/or chlorite (Gauthier-Lafaye *et al.*, 1989). During a mineralogical study of sandstones (quartz arenites) underlying a natural fission reactor at Bangombé (20 km south of the Oklo uranium deposit), we have found several grains of a uranous silicate, coffinite,