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Investigation of the physicochemical characteristics of ancient mortars by static and dynamic studies

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Abstract

The present work focuses on the investigation of physicochemical characteristics of ancient mortars through the use of static and dynamic methods. Pore structure characteristics of limestone mortars are determined by means of the mercury porosimetry technique. Preliminary results show an average pore size of >900Å, indicating the major role of macropores in the mortars. A pseudo-first order reaction–diffusion model is developed for investigating the transport and reaction of CO_2 on such samples. The model is solved for each isotope of CO_2 and the isotopic fractionation is determined as a function of distance from the surface of the mortar. The model's results are fitted to experimental data on carbon isotopic compositions obtained on these mortars. From the optimum fitted parameters, it follows that pore diffusion has a significant effect on the reaction rate of CO_2 on the structure of the ancient mortars. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Over the last decade, there has been an increased interest in the preservation of valuable ancient monuments, which tend to deteriorate through their constant contact with atmospheric pollutants. Furthermore, the study of limestone mortars is of particular interest since these are the basic building materials in the construction of ancient monuments located in several places in Greece. The dating of these materials using the radiocarbon method is of great interest to archaeologists and over the past 3 decades much research has been undertaken to the subject [1–7]. In some cases the dates found have been confirmed by historical data, while in other cases there is a considerable difference between the findings from the radiocarbon dating method and the dates indicated from historical data (see for example Ref. [3]). This emphasizes the need for a further development in the radiocarbon dating method, to incorporate such discrepancies.

When studying the variation of atmospheric CO_2 absorption in limestone mortars, one has to consider two major issues in the problem: (a) the structure of the material and (b) the transport and reaction characteristics of relevant gas species from the atmosphere to the mortar. A system of particular environmental interest is the transport and reaction of CO_2 on ancient mortars. It has been indicated by Van Strydonnck et al. [8] that isotopic fractionation (mainly the ^{18}O and ^{13}C isotopes) can provide valuable information in understanding the reaction and diffusion of CO_2 on mortars. This can further contribute to the information of the manufacture of the mortar and under data analysis using the proper mathematical model, to a correction in the dating of these mortars.

The aim of the present work is to study the transport and reaction of CO_2 on ancient Greek mortars (dated around 1500 BC) through isotopic fractionation, by combining mathematical modeling with experimental results. For this reason, the mortars are characterized using mercury porosimetry, to determine basic structural characteristics, such as pore size distribution, surface area and pore volume. Subsequently, a pseudo-first order reaction–diffusion model has been developed and solved for each isotope of CO_2, and the isotopic fractionation is determined as a function of distance from the surface of the mortar. Using standard optimization techniques the optimum reaction–diffusion parameters are

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determined by fitting the experimental data to the theoretical model. These parameters can be used to predict the isotopic fractionation at distances further away from the surface of the material.

2. Theory

The basic reactions that occur in order to obtain limestone mortar are the following Eq. (1,2,3)

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

$$CaO + 2H_2O \rightarrow Ca(OH)_2 + H_2O \quad (2)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (3)$$

It should be mentioned that the $CaCO_3$ in reaction (1) does not contain any ^{14}C. On the other hand, reaction (3) involves atmospheric CO_2 that contains traces of ^{14}C. Therefore, the amount of radiocarbon in $CaCO_3$ will be equal to that found in atmospheric CO_2 at the time the mortar was laid, ignoring any isotopic fractionation between CO_2 and $CaCO_3$ as suggested previously [9]. However, if one wants to use the radiocarbon of such calcium carbonates to obtain the exact dates of the examined mortars, one should always check that two important conditions are satisfied:

(a) reaction (1) must be complete so that no unreacted $CaCO_3$ is mixed with the one produced from reaction (3).
(b) $CaCO_3$ should have not been mixed with sea sand or fossil shells, which contain carbonate or any limestone fragments but not ^{14}C.

If one of these conditions is not satisfied, the calcium carbonate obtained at the end of the reactions (1)–(3) will contain an additional amount of carbonate that usually does not contain radiocarbon. Therefore, in such a case, the dating of the corresponding mortar will produce systematically earlier results than those expected from the historical data.

2.1. Mathematical models

Assuming that carbon in the atmospheric CO_2 contains the two isotopes, ^{13}C and ^{12}C, reaction (3) can be re-written as follows Eq. (3a,3b).

$$Ca(OH)_2 + {}^{12}CO_2 \rightarrow Ca^{12}CO_3 + H_2O \quad (3a)$$

$$Ca(OH)_2 + {}^{13}CO_2 \rightarrow Ca^{13}CO_3 + H_2O \quad (3b)$$

Considering gaseous diffusion of CO_2 isotopes through the pores of the mortar followed by a pseudo-first order reaction for each isotope, the corresponding mass balances for $^{12}CO_2$ and $^{13}CO_2$ are:

$$\frac{\partial[{}^iCO_2]}{\partial t} = \nabla D_i \nabla[{}^iCO_2] - k_i[{}^iCO_2] \qquad i = 12, 13 \quad (4)$$

where k_{12} and k_{13} are the corresponding kinetic constants for reactions (3a) and (3b), respectively. Eq. (4) can be simplified considerably by making the realistic assumptions that the main resistance to CO_2 diffusion is normal to the mortar surface [10] and that CO_2 is at steady state, considering the fact that experimental measurements are obtained several thousand of years after the start of the above process. Therefore, Eq. (4) becomes Eq. (5):

$$D_i \frac{\partial^2[{}^iCO_2]}{\partial z^2} - k_i[{}^iCO_2] = 0 \qquad i = 12, 13. \quad (5)$$

The corresponding boundary conditions for the above set of differential equations are the following Eq. (6a,6b).

$$z = 0 \qquad [{}^iCO_2] = [{}^iCO_2]_{\text{surface}} \qquad i = 12, 13 \quad (6a)$$

$$z = L \qquad \frac{\partial[{}^iCO_2]}{\partial z} = 0 \qquad i = 12, 13 \quad (6b)$$

In the above equations, we assumed that CO_2 diffusivities are constant, an assumption which is not always valid. In fact, the presence of moisture inside the porous matrix can significantly hamper the diffusion of gases as has been shown elsewhere [11,12].

The above set of ordinary differential equations can be solved analytically (see for example Ref. [13]) to give:

$$[{}^iCO_2] = [{}^iCO_2]_{\text{surface}} \cosh\left\{\Phi_i\left(1 - \frac{z}{L}\right)\right\} / \cosh(\Phi_i) \qquad i = 12, 13 \quad (7)$$

where $\Phi_i=(k_iL^2/D_i)^{\{1/2\}}$, i=12,13 are the corresponding Thiele moduli for first order reactions. The Thiele modulus is a standard dimensionless number used in reaction engineering and determines the effect of pore diffusion in the reaction rate [10]. If this number is normally much less than unity then diffusion has no significant effect on the reaction process. If, on the other hand, the Thiele modulus is large, then diffusional resistance plays a major role in the reaction process.

From Eq. (7), the isotopic ratio $R=[^{13}CO_2]/[^{12}CO_2]$ becomes:

$$R(z) = R_{\text{surface}} \frac{\cosh\left\{\Phi_{13}\left(1 - \frac{z}{L}\right)\right\}\cosh(\Phi_{12})}{\cosh\left\{\Phi_{12}\left(1 - \frac{z}{L}\right)\right\}\cosh(\Phi_{13})}. \quad (8)$$

Eq. (8) gives the isotopic fraction for CO_2 at different distances from the surface of the mortar as a function of the isotopic fraction at the surface, and the Thiele moduli of the isotopes. If, in addition, the assumption of no fossilized carbonate (either from unreacted $CaCO_3$, or any other source) in the product is valid, then the above ratio should be also equal to the isotopic ratio of $CaCO_3$ that is measured experimentally. Since the Thiele modulus expresses the ratio of the diffusive over the kinetic resistance to transport, by fitting the experimental data one can draw conclusions for the transport and reaction mechanism of CO_2 in the mortar.

3. Experimental

3.1. Selection of samples

In the present study, samples from different places in Greece were chosen from the Mycenaean and Minoan age. The mortars chosen had been used as supports for paintings with well-defined chronological age. Furthermore, the majority of these mortars contained no quartz impurities, indicating the absence of sea sand or crushed fossil shells in the preparation of the mortar.

All the samples that were analyzed weighted around 10–12 g and had a painted surface between 1 and 3 cm^2. Before measurement, the samples were cleaned with a very dilute solution of HCl (0.1%) in an ultrasonic bath.

3.2. Pore structure characterization using Hg porosimetry

Mercury porosimetry is a simple, quite inexpensive, relatively fast method and can give valuable information about the pore volume, surface area and pore size distribution of the materials [14]. The only limitation of the method is that it is applicable to macroporous materials with average pore sizes above 500 Å [14]. For materials with small pores—in the mesopore (between 20 and 500 Å) or in the micropore region (below 20 Å)—other methods such as liquid N_2 or Ar porosimetry should be employed. Although it has been shown that such mortars contain a non-negligible amount of mesopores [15], the majority of pores in these mortars is expected to be in the macropore region. Thus, it was decided to employ only Hg porosimetry in this work.

The method involves evacuation of the volume containing the sample. Mercury is then transferred into the sample container while under vacuum. Finally, pressure is applied to force Hg into the pores. The intruded volume, if plotted versus pressure, gives the "intrusion curve." Intrusion pressure is related to the pore radius in which Hg intrudes by the Laplace equation:

$$P = -2\gamma\cos\theta/r \tag{9}$$

where γ is the surface tension of Hg and θ is the contact angle. The same equation [Eq. (9)] holds for extrusion too. Thus, pore size distributions can be obtained by the intrusion–extrusion curves [16].

3.3. Measurement of isotopic compositions

The carbon isotopic compositions have been measured using a triple collector mass spectrometer (Isogas, type SIRA 9). Details on the experimental procedure are given elsewhere [9]. The isotopic compositions are expressed in δ‰ units as follows in Eq. (10):

$$\delta = (R_{\text{sample}}/R_{\text{reference}} - 1)10^3 \tag{10}$$

where $R$is the isotopic fraction defined in the theoretical section above. The reference standard used is the PDB [17]. The atmospheric CO_2 had a value of $\delta^{13}C$ close to −6.5‰ with respect to PDB.

4. Results and discussion

The mineralogical analysis of the mortars showed that the samples contain pure calcite with no quartz impurities. Nevertheless, samples from Knossos, Crete, have been found to contain small amounts of quartz and illite.

4.1. Pore structure characterization

Hg porosimetry has been employed to the examined samples in order to extract preliminary information on the pore structure and the fabrication technique of these mortars. The results from the measurements are summarized in Table 1. Unfortunately, not all the samples analyzed for isotopic composition are treated with mercury porosimetry. This is because of the lack of samples, since the main disadvantage of Hg porosimetry is that the sample is destroyed after an experimental cycle [16]. Fig. 1 presents the extrusion curves for the samples referred in Table 1.

When looking at the bulk densities we see that these are all below 2.1 g/cm^3. This verifies the absence of sea sand (since the density of SiO_2 is 2.5 g/cm^3). In addition, we notice that all samples show a pore size of >900 Å indicating that even if moisture is present in such pores, it would not have a major effect in the diffusion of CO_2, unless smaller pores exist (below 200 Å) which can, under proper conditions, block the pores. Since this cannot be determined by the current method, further work will be conducted using N_2 porosimetry to check for pores in the mesopore range.

Table 1
Physicochemical characteristics of the samples examined in this work

Sample	Historical period (BC)	Bulk density (g/cm^3)	Apparent density (g/cm^3)	Pore volume (mm/g)	Mean pore diameter (A)	Specific surface (m^2/g)
Pylos	1500	1.68	1.9	72.8	2000	2.26
Vergina	200	2.05	2.15	62.5	2000	2.71
Thira	1500	1.78	2.02	68.5	900	3.12

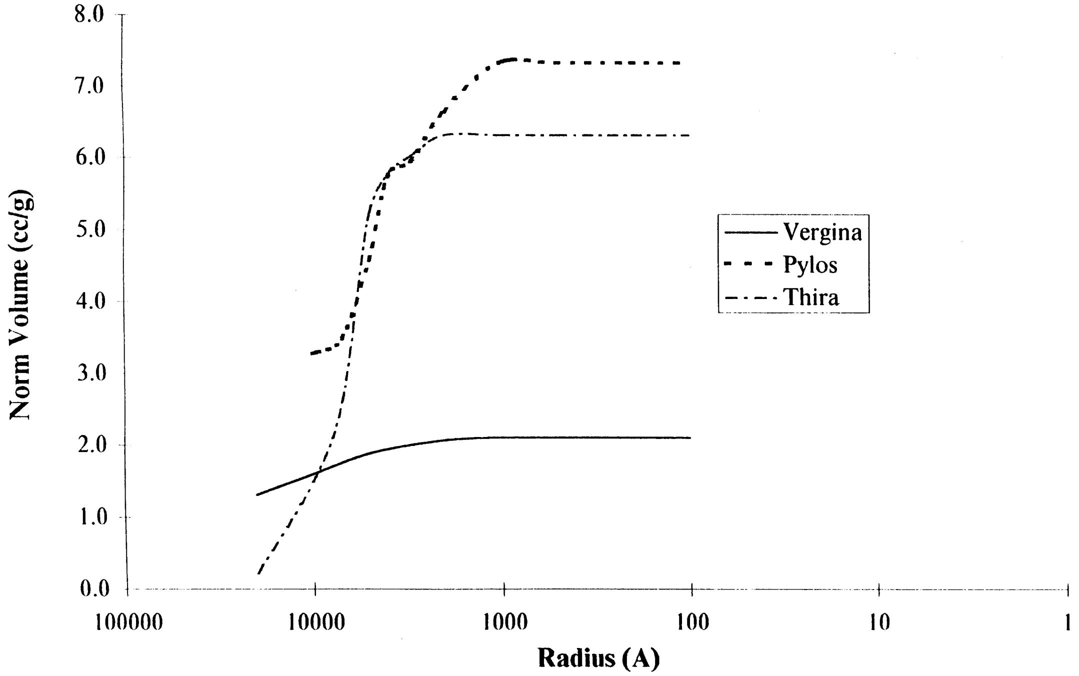

Fig. 1. Pore size distributions of ancient mortars calculated from extrusion mercury porosimetry measurements.

4.2. Determination of isotopic compositions

The carbon isotopic fractions in the carbonate of mortars have been measured to study the transport and reaction mechanism of CO_2 in the pores of the mortar. In addition, these measurements might evidence a possible mixing between the $CaCO_3$ generated during reaction (3) and a residual/or added sedimentary carbonate.

The $\delta^{13}C$ values of a carbonate depend on various parameters, such as the temperature of the reaction, the

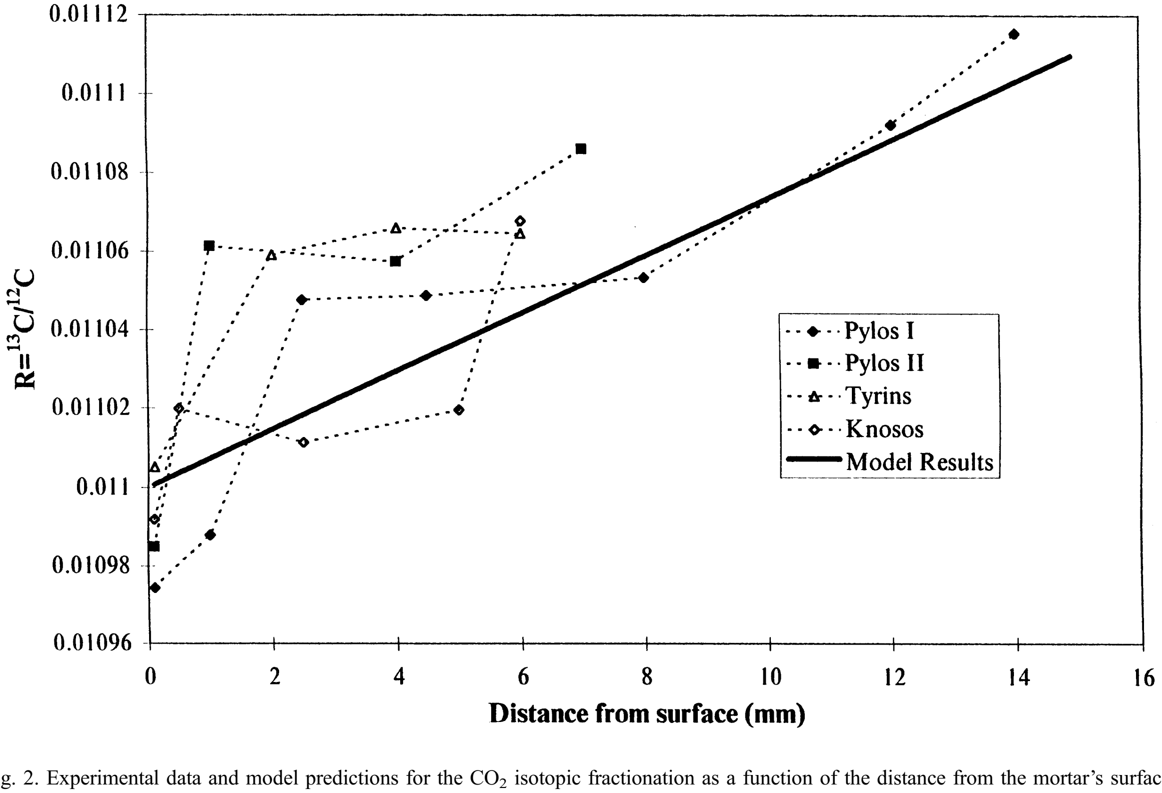

Fig. 2. Experimental data and model predictions for the CO_2 isotopic fractionation as a function of the distance from the mortar's surface.

isotopic composition of the atmospheric CO_2, and on the reaction and diffusion characteristics of CO_2 isotopes in the pores of the mortar.

Experimental results from several mortars are presented in Fig. 2. In order to transform the experimental δvalues to R values, $R_{\text{reference}}$ was estimated to be equal to 0.011198. This value was calculated from the relative concentration of the atmospheric CO_2 in the two isotopes ^{12}C and ^{13}C, which is $R_{\text{atm}} = 1.1/98.9$. As one can see from Fig. 2, experimental data for R from different samples show similar trend as a function of the distance from the surface. In order to obtain a "master curve" that fits well all the data, a constant value for $R_{\text{surface}} = 0.011$ is assumed. In addition, a reasonable thickness of the construction is $2L = 0.4$ m. With these values, a good fit of the experimental data is obtained by setting $D_{12}/K_{12} = 0.066$ and $D_{13}/k_{13} = 0.09$. In Fig. 2, model predictions with these parameters are shown. It is well known [10] that for an isotopic pair ($^{12}C-^{13}C$ in this case), the ratio of diffusivities is given to a very good approximation from the expression Eq. (11):

$$\frac{D_{13}}{D_{12}} = \sqrt{\frac{MW_{^{12}CO_2}}{MW_{^{13}CO_2}}} \tag{11}$$

and so Eq. (12):

$$\frac{k_{12}}{k_{13}} = 1.349 \tag{12}$$

which means that the rate constant for the reaction of $^{12}CO_2$ is approximately 35% higher than the rate constant for the reaction of $^{13}CO_2$. Note that the corresponding Thiele modulus values are $\Phi_{12} = 0.7785$ and $\Phi_{13} = 0.6667$, denoting a non-negligible effect of pore diffusion in the reaction rate.

5. Conclusions

Ancient Greek mortars from the Mycenaean and Minoan age were examined in the present study in terms of their physicochemical characteristics. Experimental techniques together with mathematical models were been employed for this purpose.

Pore structural properties of these mortars were determined using Hg porosimetry. It was found that the majority of the measured samples have densities below 2 g/cm^3, indicating the absence of sea sand in the mortar preparation procedure. Furthermore, all samples showed an average pore size of >900 Å, indicating the major role of macropores in the pore structure. Nevertheless, additional techniques such as N_2 porosimetry should be employed to check for the possible existence of mesopores or micropores in the structure.

A pseudo-first order reaction–diffusion model was developed to study the transport and reaction of CO_2 on the samples. The model was solved for each isotope of CO_2 and the isotopic fractionation was determined as a function of distance from the surface of the mortar. The model results are in agreement with the trend that the isotopic CO_2 ratio follows with the distance from the mortar's surface. Isotopic composition increases as one moves away from the surface into the inner part of the sample. Nevertheless, it is clear that the actual mechanism followed is more complicated than the one assumed in the model.

The theoretical results are fitted to experimental data on carbon isotopic compositions obtained from these mortars. It is found that the optimum kinetic and diffusive parameters obtained from the model correspond to Thiele moduli around unity, indicating the significant contribution of pore diffusion in the reaction rate of CO_2 in the structure of the mortar.

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