

A hydrous Ca-bearing magnesium carbonate from playa lake sediments, Salines Lake, Spain

IGNASI QUERALT,¹ RAMON JULIÁ,¹ FELICIANO PLANA,¹ AND JAMES L. BISCHOFF²

¹Institute of Earth Sciences “Jaume Almera” (CSIC), Solé Sabarís s/n, 08028, Barcelona, Spain

²U.S. Geological Survey MS 999, 345 Middlefield Road, Menlo Park, California 94025 U.S.A.

ABSTRACT

Sediments of playa Lake Salines, SE, Spain, contain a carbonate mineral characterized by X-ray diffraction peaks very similar to, but systematically shifted from those of pure magnesite. Analyses (SEM, IR and Raman spectroscopy, DTA, TGA, and ICP) indicate the mineral is a hydrous Ca-bearing magnesium carbonate with the chemical formula $(\text{Mg}_{0.92}, \text{Ca}_{0.08})\text{CO}_3 \cdot 3\text{H}_2\text{O}$. Thermal characteristics of the mineral are similar to those of other known hydrated magnesium carbonates. X-ray and electron diffraction data suggests a monoclinic system ($P21/n$ space group) with unit-cell parameters of $a = 6.063(6)$, $b = 10.668(5)$, and $c = 6.014(4)$ Å and $\beta = 107.28^\circ$.

INTRODUCTION

Although much rarer than the various forms of CaCO_3 , magnesium carbonates have been reported in sediments of several saline lake systems (Alderman and Skinner 1957; Hardie 1987; Gunatilaka 1987; De Deckker and Last 1988; Last 1993). The difficulties involved in separating pure phases from fine-grained polymineralic sediments, however, have discouraged detailed studies of these minerals. We report here on the occurrence and paragenesis of a hydrous Ca-rich magnesium carbonate (abbreviated hereafter as HCMC) recently recovered from two saline lakes in eastern Spain. This part of the Iberian Peninsula contains one of the most extensive areas of saline lakes in Europe.

GEOLOGICAL SETTING

Salines is a playa lake that occupies a hydrographically closed basin at the foot of the southeastern escarpment of the Sierra de Salines. The lake basin is bounded by the Salines and Cabrera ranges, the eastern terminus of the Alpine Betic Chain of the Iberian Peninsula (Fig. 1). Bedrock of these ranges is primarily Mesozoic marine limestone, dolostone, and gypsum, overlain by Paleogene and Neogene continental and marine sedimentary rocks. Extensive alluvial fans span the area between the ranges and the playa surface, which itself covers an area of 1.6 km² at an elevation of 475 m. The catchment area includes about 71.2 km² and extends to an elevation of 1047 m. With a mean annual precipitation of 350 mm, annual temperatures of about 14 °C, and an evapotranspiration rate of about 1500 mm, the area is characterized as having a xeric Mediterranean climate.

Historical data (archives of the city of Salines) reveal that the lake level and salinity have undergone wide fluctuations because of human activity during the last 400 years. These activities include brine extraction and graz-

ing and farming of the surrounding area. The most drastic change in the water balance culminated between 1940 and 1950 when five wells were drilled to extract 12000 m³/day. Since that time, the lake has refilled only occasionally and is now mostly dry but temporarily contains water during the rainy season.

OCCURRENCE AND SAMPLING

The HCMC was first detected in several different sedimentary horizons within the top two meters of a 40 m drill core in Salines Lake (Fig. 2) and was also later identified in surface sediments of Gallocanta Playa in the central part of Spain. This present study focuses on samples from Salines Lake drill core. The first recognition of this mineral probably was made by Graf et al. (1961), who detected a mineral with nearly identical properties in sediments of Lake Bonneville but did not investigate its composition, structure, and paragenesis.

The drill core consists of well-bedded and fine-grained mixtures of calcite, Mg-calcite, aragonite, dolomite, HCMC, quartz, halite, illite, gypsum, and celestine. In several places, large diagenetic gypsum crystals cut across the primary sedimentary structures. Samples of the sediments were taken every 3 cm along the length of the core and were air-dried. A radiocarbon date of 8570 ± 70 yr. B.P. (measured at the radiocarbon laboratory of Beta Analytic Inc. Miami, Florida, Beta-62417, CAMS-6513) taken from 2.7 m depth indicates that all HCMC occurrences are younger than this.

LABORATORY PROCEDURES

Bulk samples were first analyzed by X-ray diffraction (XRD). HCMC was found to be most abundant between 1.4 and 1.7 m (Fig. 2) where it makes up as much as 20 wt% of the sediment, coexisting with dolomite (40–75 wt%), quartz (2–6 wt%), halite (9–16 wt%), illite (1–5

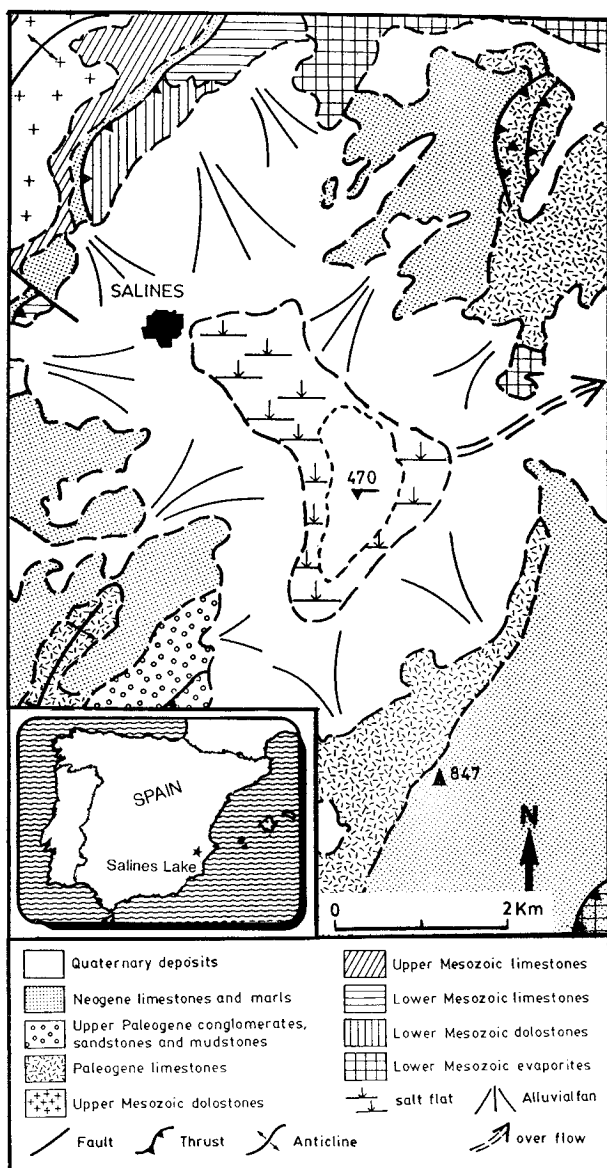


FIGURE 1. Geological map of Salines Lake area.

wt%), gypsum (0–6 wt%), and celestine (0–7 wt%). These percentages were calculated using the quantitative XRD procedures of Chung (1974).

It was not physically possible to separate or isolate pure HCMC from the sediment matrix because of the extremely fine grain size. For this reason, selective leaching was used because the rate of dissolution of magnesium carbonate is several orders of magnitude lower than that of other single carbonates (Chou et al. 1989). HCMC was concentrated from the bulk samples using procedures similar to those used by Graf et al. (1961) to concentrate magnesium carbonate phases from Lake Bonneville sediments. Samples were leached with 0.5% HCl solution for 4 h. During this process, calcite, dolomite, halite, and gypsum were completely dissolved. The residue was then

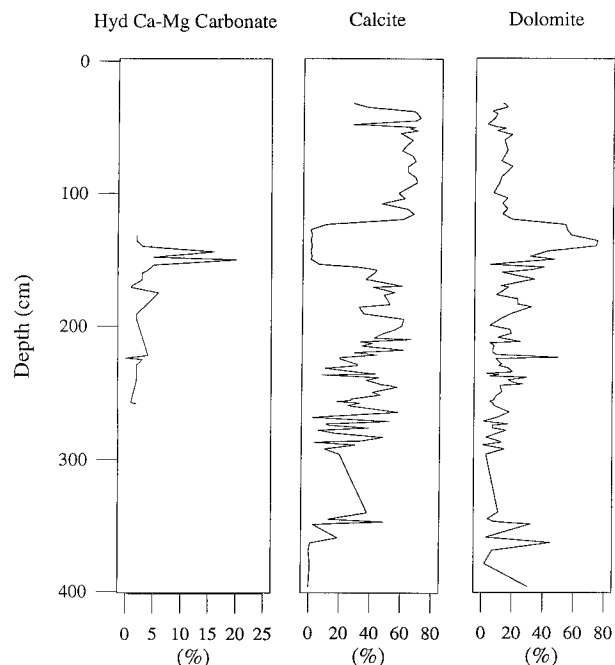


FIGURE 2. Distribution of carbonate minerals along the core stratigraphic sequence.

collected by filtration and repeatedly washed with distilled water. XRD revealed that the residue contained HCMC and 4–10% quartz impurities. We found that using longer leaching times or more concentrated HCl resulted in the complete disappearance of HCMC.

The XRD scans were carried out using an automated Siemens D500 diffractometer (copper tube operating at 40 kV, 30 mA, graphite monochromator, 0.02° step scan resolution). X-ray fluorescence analyses (XRF) were carried out on a Rigaku SMAX spectrometer (rhodium tube, LiF 200 and 220 analyzer). Inductively coupled plasma (ICP-AES) analyses were carried out by means of a Jobin Yvon JY 38-VHR spectrometer. Microprobe analyses were performed using a Cameca Camebax SX50 (both optical and electron microscopes). The infrared (IR) spectra were obtained using a Bomem Fourier transform spectrometer (model MB-120, 400–5000 cm⁻¹, 1 cm⁻¹ resolution). Raman spectra were obtained from a Jobin Yvon T64000 spectrometer (argon laser source and microscope for Raman microprobe analyses). Electron diffraction patterns of single particles were obtained using a Philips transmission electron microscope (TEM). Scanning electron microscopy (SEM) was carried out on a Jeol J6400 (which includes XRF analysis by EDAX with a Link-4 analyzer). Differential thermal analyses (DTA) and thermogravimetry analysis (TGA) were carried out on a Perkin Elmer thermoanalyser (5 and 15 °C/min, 25–1000 °C). DTA-TGA samples obtained in each 50 ° step were analyzed by XRD to identify the by-products. Chemical analyses were performed on bulk samples, and on the leached residues by XRF and SEM-XRF and by ICP.

TABLE 1. Chemical composition of HCMC from Salines Lake

| | ICP-AES* (micrograms/gram) | | | | | EDX-SEM | |
|----------|----------------------------|--------|--------|--------|-----------|-------------|-------|
| | A | B | C | Mean | Error (%) | Element (%) | Mean |
| Mg | 157.59 | 157.79 | 157.57 | 157.65 | 0.40 | 20.9–22.1 | 21.8 |
| Ca | 22.52 | 22.50 | 22.33 | 22.45 | 0.55 | 3.0–3.4 | 3.12 |
| Mg:Ca | 7.000 | 7.010 | 7.056 | 7.023 | | | 6.987 |
| <i>n</i> | 4 | 4 | 4 | | | 15 | 15 |

* Analyses were carried out using three different solutions (A, B, C). *n* = number of analyses.

RESULTS

Chemical composition

Chemical analyses of the bulk samples and of the leached residues were performed by EDX-SEM and by ICP (see Table 1). Only Mg, Ca, and minor Si were detected, with a mean Mg:Ca ratio of 7.023, suggesting a 11.5 mole ratio of $MgCO_3$ to $CaCO_3$ in HCMC. The sum of Mg and Ca carbonate, however, accounts for only 61–62% of the total mass. The absence of other cations, together with the results from IR and Raman spectral analyses, suggests the missing mass is structural H_2O . This conclusion is corroborated by the weight loss observed on ignition and by TGA. The results indicate there are three molecules of H_2O per formula unit of HCMC, yielding a stoichiometry of $(Mg_{0.92}, Ca_{0.08})CO_3 \cdot 3H_2O$.

Infrared spectroscopy

Infrared spectra have proven useful for the analysis of carbonate minerals (White 1976). In the IR spectra of the bulk sample (Fig. 3a), peaks at 877 and 729 cm^{-1} are characteristics of dolomite. In the leached samples with HCMC as the only remaining carbonate (Fig. 3b) peaks are seen at 885 and 746 cm^{-1} , close to the theoretical position for magnesite (Van der Marel and Beutelspacher 1976), and the intense band around 1020 cm^{-1} is ascribed to quartz impurities. The broad band in the 3800–3000 cm^{-1} region is common to the spectra of both the bulk and leached samples (Fig. 3), and its greater intensity in the latter is attributed to the structural water in HCMC. This band does not occur in spectra of pure anhydrous carbonates. The hydroxyl and H_2O -stretching region near

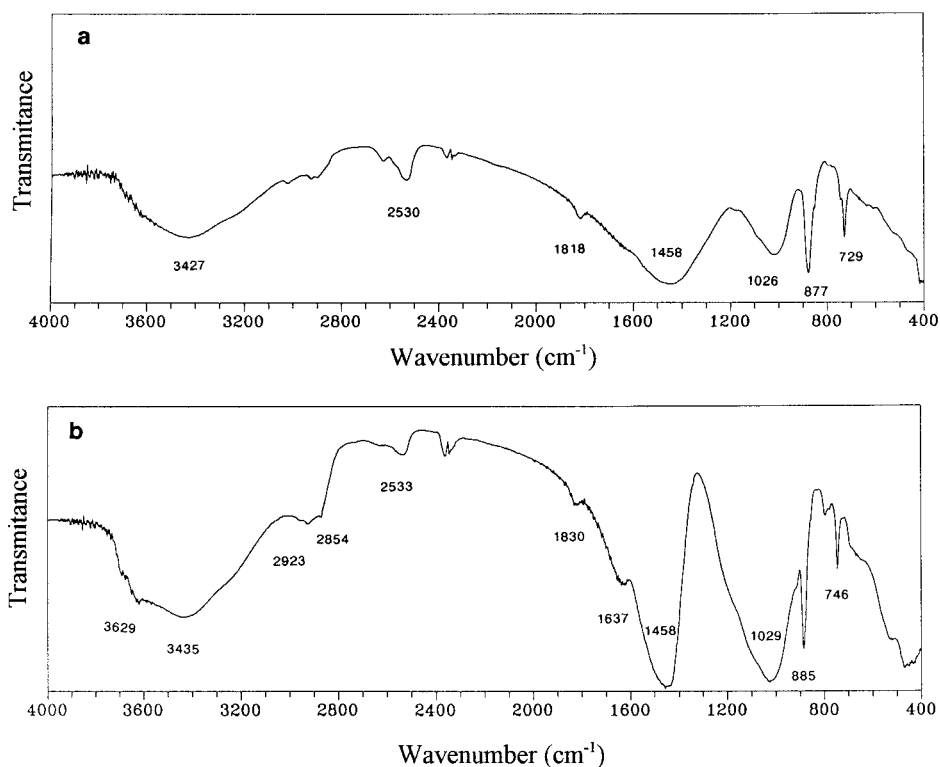


FIGURE 3. Infrared spectra plots of Salines Lake sediments. (a) Whole dolomitic sediment. (b) Hydrous Ca-bearing Magnesium Carbonate (HCMC).

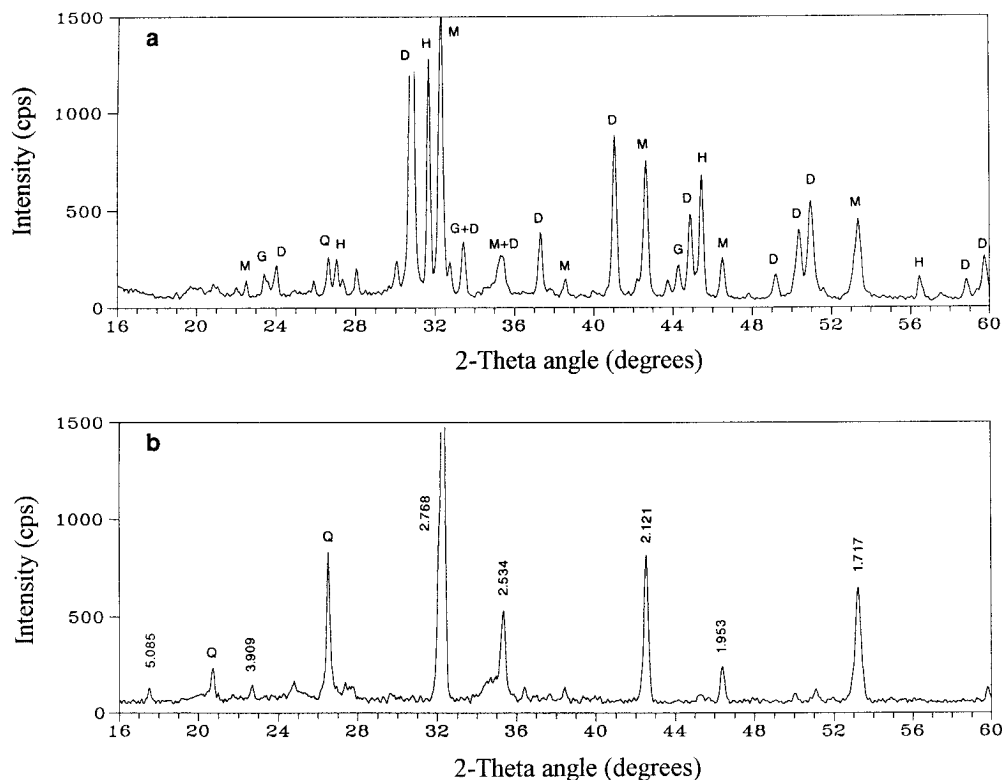


FIGURE 4. X-ray diffraction plots of Salines Lake sediments (sampling depth level, 1.50 m). (a) Whole sediment, (b) Residue of acid treatment, showing the major diffraction peaks (basal d) for the hydrocamagite. M = HCMC, G = gypsum, D = dolomite, H = halite, Q = quartz.

3200 cm^{-1} for most hydrated carbonates usually consists of one or two broad bands shifted somewhat to lower frequencies because of hydrogen bonding. In this region, spectra of hydrous magnesium carbonates (artinite, lansfordite, hydromagnesite, and nesquehonite) have one or more very sharp bands whose position differs from one mineral to another, and which can be used to distinguish between these minerals. These bands have been interpreted to indicate different kinds of OH and H_2O groups in this mineral family, some participating in hydrogen bonding and others not. In the present case, the IR spectrum for HCMC showed a broad band centered around 3435 cm^{-1} and a sharp band at 3629 cm^{-1} that is very similar to the spectrum of nesquehonite (broad band at 3430 cm^{-1} and sharp band at 3658 cm^{-1} , according to White 1976).

X-ray diffraction

Peaks for dolomite, HCMC, halite, and small amounts of quartz are shown on the XRD spectrum of the bulk sample, whereas only peaks for HCMC and small quantities of quartz are shown in the spectrum of the leached sample (Figs. 4a and 4b). As a first approximation, the peak positions and relative intensities of HCMC show a significant similarity to those of magnesite, with peaks systematically shifted to lower 2θ angles. Moreover, the

HCMC diffractogram does not correspond to any of those of the hydrous magnesium carbonates listed in the JCPDS catalogue.

Electron microscopy

SEM observations of bulk samples show dominance of dolomite in two forms: (1) well-crystallized dolomite, exhibiting the typical rhombohedral forms of 2 to $15\text{ }\mu\text{m}$ and (2) dolomite in fine aggregates of $> 3\text{ }\mu\text{m}$. The latter, in many cases, is seen deposited on the surfaces of the former (Fig. 5a) suggesting a secondary origin. The average Mg content of the fine dolomite aggregates, measured by EDAX is $51.5 \pm 0.9\text{ atom\%}$ and 48.5 ± 0.7 for the Ca content, analogous to the "slightly Mg-rich dolomite" described by Last and De Deckker (1990) in the saline volcanic maar lakes of Victoria, Australia. In contrast, the rhombohedral forms display a nearly 1:1 stoichiometric ratio of Mg to Ca. SEM observations on the leached sample (Fig. 5b) show an abundance of crystals of fibrous morphology, $0.5\text{--}10\text{ }\mu\text{m}$ long. EDX analysis indicates a MgCO_3 content ranging between 84 to 91 mol%, values comparable to, but slightly lower than those obtained by ICP-AES. The fibrous morphology, however, does not lend itself for highly accurate EDAX analysis.

From the point electron diffraction patterns obtained by transmission electron microscopy (Fig. 6) it is possible



FIGURE 5. (a) Calcium rich dolomite. (b) HCMC fiber-like forms.

to obtain two clear dimensions from the observed reciprocal lattice. Using procedures of Macicek (1992), we calculate 6.04 ± 0.15 and 5.95 ± 0.17 Å for the cell parameters of HCMC.

Raman spectroscopy

The Raman spectra of calcium and magnesium carbonates at ambient conditions are well characterized (Rutt and Nicola 1974; Williams et al. 1992). Vibrational modes for calcite, dolomite, and magnesite are well-known (Bischoff et al. 1985; Gillet et al. 1993). HCMC (Fig. 7) exhibits peaks identical to dolomite (173, 296, 1096, and 1438 cm^{-1}), confirming that both Ca and Mg may be present in similar coordination geometry as they are in dolomite. HCMC also exhibits a broad band in the region of 3300–3700 cm^{-1} with superimposed sharp peaks at 3361, 3408, and 3601 cm^{-1} , which are attributed to H_2O in the structure.

Structural considerations

The presence of H_2O in HCMC complicates the complete characterization and solution of its crystal structure. We were unable to isolate single crystals from the bulk

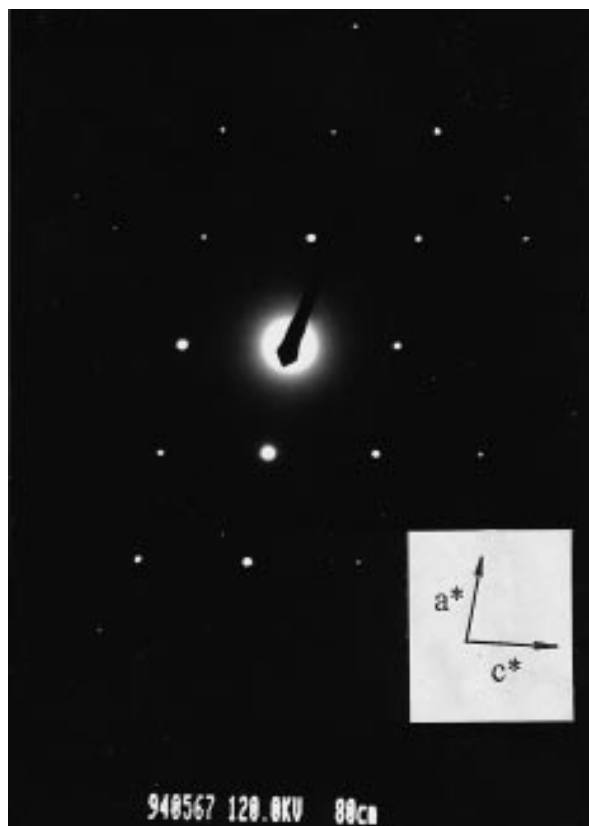


FIGURE 6. Electron diffraction pattern of HCMC.

sediment to perform an accurate structural study, and attempts at laboratory synthesis were unsuccessful. We used empirical computing matching programs for indexing of powder diffraction patterns (Louer and Louer 1972; Werner 1984; Boulif and Louer 1991) and found no good match in the hexagonal or rhombohedral systems. Several solutions, however, were found in the monoclinic system, which includes all the hydrated and basic magnesium carbonates (Akao et al. 1974; Stephan and MacGillavry 1972).

The best fit monoclinic cell, compatible with the electron diffraction pattern, and the corresponding cell parameters for HCMC, following Appleman-Evans refinement method (Benoit 1987) yields cell parameters, $a = 6.063(6)$, $b = 10.668(5)$, and $c = 6.014(4)$ Å, and $\beta = 107.28$ degrees. Although the values of a and c are close to the true rhombohedral parameters of the anhydrous carbonates (6.37 Å for calcite, 6.02 Å for dolomite and 5.67 Å for magnesite), the cell volume of 371 Å³ is considerable greater than those of magnesite (279 Å³) and dolomite (320.9 Å³). These relations suggest an expanded (one enlarged cell parameter) and distorted cell but with certain traits of the anhydrous carbonates. The indexing of the basal values of d (Table 2) and the corresponding intensities allow us to assign the structure to the $P21/n$ space group.

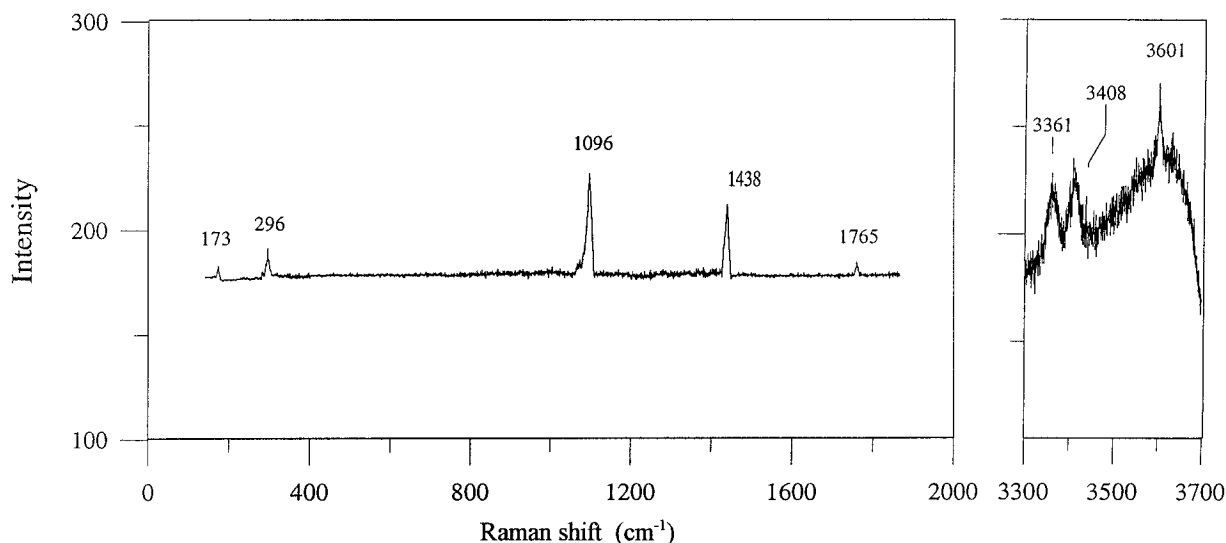


FIGURE 7. Raman spectra plot of HCMC.

Thermal behavior

Thermal behavior of magnesium and calcium carbonates are well-known from the compilations of Webb and Krüger (1970) and Smykatz-Kloss (1974). For these compounds, the endothermic decomposition with the liberation of CO_2 is the most characteristic property. The temperatures of CO_2 liberation for anhydrous carbonates are in the range from 650° to 900 °C. In contrast, thermal decomposition of hydrated and basic magnesium carbonates always occurs at temperatures < 600 °C. Only huntite shows a slightly higher temperature for decomposition (600° to 630 °C). All hydrated forms of magnesium carbonate exhibit at least two clear endothermic effects. The first, occurring from 200° to 450 °C, has been classically attributed to the loss of structural H_2O , and the second, from 500 to 600 °C, to liberation of CO_2 . In the DTA and TGA plots of HCMC (Fig. 8) two main effects were seen at 455° and at 630 °C. The TG plot shows a continuous weight loss up to 425°, followed by a second starting at 520 °C and terminating at 600 °C.

XRD monitoring of the HCMC charge at 50 °C increments shows that it remains unaltered up to 400 °C, decomposing between 400 ° and 450 °C, and yielding a final residue of periclase (MgO) and a minor quantity of lime (CaO).

DISCUSSION AND CONCLUSIONS

The most common occurrence of anhydrous magnesium-carbonates is as an alteration mineral of Mg-rich igneous and metamorphic rocks and as a result of Mg metasomatism of preexisting sediments. Its occurrence in precipitates from saline lake waters has only recently been noted.

At present, eight hydrated magnesium carbonate minerals are listed in the JCPDS (1991) mineral database (artinite, hydromagnesite, barringtonite, nesquehonite,

lansfordite, dypingite, giorgiosite, and pokrovskite). These minerals are accurately distinguished from one another by their IR spectra (as was reported by White 1976) and XRD. The IR vibrational bands of all the minerals of this group are markedly different from those of the Salines Lake HCMC. All these minerals have monoclinic structure, different from the minerals belonging to the calcite group. HCMC presents XRD powder plot with peak intensities and peak position similar to, but systematically shifted from than those reported for pure magnesite.

The occurrence of a variety of magnesium carbonate minerals in lake sediments has been widely observed recently. In Australian saline lakes, for example, Last and De Deckker (1990) found dolomite [$\text{CaMg}(\text{CO}_3)_2$], hydromagnesite [$4\text{MgCO}_3\text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], magnesite

TABLE 2. X-ray powder-diffraction data for HCMC from Salines Lake (Spain) indexed according to the monoclinic space group $P2_1/n$

| d_{obs} (Å) | d_{calc} (Å) | hkl | I/I_0 |
|----------------------|-----------------------|-------|---------|
| 5.085 | 5.086 | 110 | 6 |
| 3.909 | 3.907 | 021 | 9 |
| 3.575 | 3.576 | 101 | 11 |
| 2.768 | 2.771 | 012 | 100 |
| 2.530 | 2.527 | 022 | 23 |
| 2.433 | 2.432 | 202 | 6 |
| 2.337 | 2.338 | 141 | 8 |
| 2.121 | 2.120 | 122 | 38 |
| 2.003 | 2.003 | 103 | 6 |
| 1.953 | 1.954 | 042 | 13 |
| 1.786 | 1.788 | 202 | 7 |
| 1.717 | 1.717 | 250 | 30 |
| 1.674 | 1.674 | 103 | 3 |
| 1.520 | 1.521 | 331 | 4 |
| 1.499 | 1.498 | 411 | 7 |
| 1.416 | 1.417 | 143 | 6 |
| 1.366 | 1.366 | 223 | 5 |
| 1.347 | 1.346 | 072 | 5 |
| 1.264 | 1.264 | 044 | 3 |
| 1.248 | 1.249 | 181 | 2 |

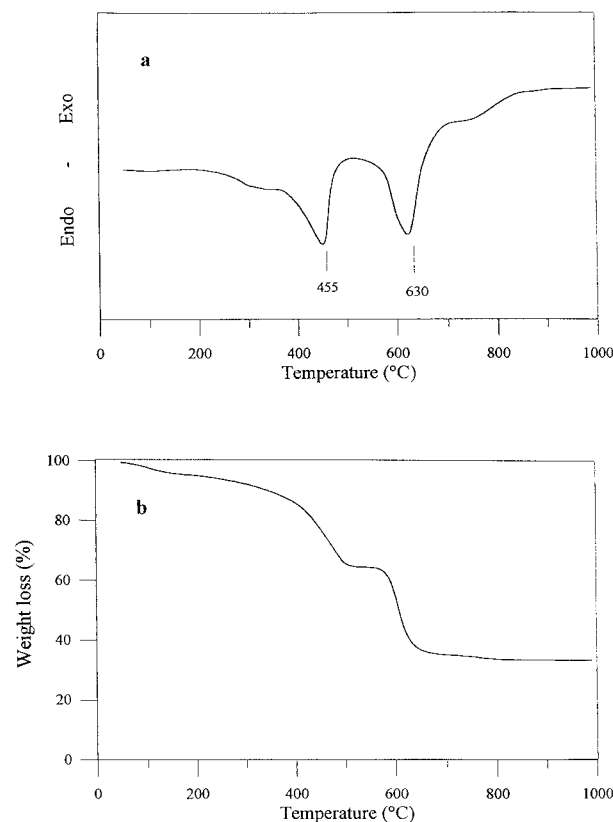


FIGURE 8. (a) Differential thermal analysis of HCMC. (b) Thermogravimetric analysis of HCMC.

(MgCO_3), and “protohydromagnesite” ($\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$). They concluded that the high Mg/Ca ratio of the water is the control on the precipitation of dolomite and hydromagnesite. The occurrence of dolomite-magnesite minerals in other lake sediments seems to be predicted by elevated Mg/Ca ratios.

Although the occurrence of nonstoichiometric calcite and dolomite is well documented, we have found no previous reports of calcium substitution in the structure of magnesite or of Ca substitution into “protohydromagnesite,” the more approximate phase (from paragenetic and a chemical point of view) to the HCMC in the Salines Lake (see Last and De Decker 1990).

The general paucity of detailed chemical analyses of many naturally occurring carbonate minerals, as pointed out by Reeder (1990), may be attributed to an assumed stoichiometric simplicity of carbonates. The present study suggests that site distributions in naturally occurring hydrous carbonates should be more vigorously explored.

The diffraction peaks position and the Mg/Ca ratio of the Salines Lake HCMC from various samples are always closely similar, which suggests that substitution in the magnesite structure is governed and limited by structural factors. Its occurrence in restricted sedimentary horizons suggests that HCMC results from chemical precipitation in restricted and unusual chemical conditions. Its associ-

ation with the slightly nonstoichiometric dolomite, suggests a possible paragenetic relationship.

We suggest that HCMC may be a common phase in saline lake sediments and that it can be accurately identified using its unique X-ray diffraction pattern. We have detected it in 22 stratigraphic horizons of the recent sediments of Salines Lake and also in Gallocanta Lake sediments and found no variations of the attributed major XRD peaks. This observation suggest to us it is an identifiable discrete mineral phase in depositional saline lake environment.

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