Vaterite Stability in the Presence of Chromate

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ABSTRACT Vaterite aggregates grown in Cr(VI)-bearing silica gel were studied by combining scanning electron microscopy and Raman spectroscopy. All the vaterite samples were spherical aggregates consisting of lens-shaped individuals, and their morphology was distinctive for vaterite. Raman spectra corresponding to the aggregates grown in gels containing high Cr(VI) concentrations showed the typical bands of vaterite. However, in contrast to their morphology, the Raman spectra of the aggregates grown in the presence of lower Cr(VI) concentrations exclusively showed bands characteristic of calcite. These aggregates are interpreted as calcite pseudomorphs formed after vaterite through a replacement process. The replacement involves the interface coupling of the dissolution of vaterite and the precipitation of the stable polymorph calcite. The fact that only those vaterite aggregates formed in the presence of low Cr(VI) concentrations transformed into calcite indicates the presence of high Cr(VI) concentrations in the growth medium contributes to stabilize vaterite and prevents its transformation into calcite in the short term.

KEYWORDS calcite, polymorph, Raman spectroscopy, replacement, vaterite

INTRODUCTION

The crystallization of calcium carbonate is a topic relevant to numerous scientific disciplines due to the wide range of industrial applications of calcium carbonate phases and their abundance in natural environments. Although calcite is the stable calcium carbonate polymorph under Earth sur-face conditions, the formation of other less stable phases, such as aragonite and vaterite, often occurs. Metastable crystallization is commonly interpreted as due to the predominance of kinetic factors over thermodynamics under certain conditions, for example, high supersaturation.[1,2] Less stable poly-morphs most commonly transform into the stable phase. In the particular case of the calcium carbonate polymorphs calcite, aragonite, and vaterite, it has been pointed out that their free energies are close enough such that changes in the concentration of impurities incorporated into their structures can determine stability crossovers.[3] In such a case, the presence of certain ions in the growth medium can determine the stabilization of unexpected polymorphs since their incorporation into the crystal structure of these polymorphs is energetically more favorable.[4] A recent experimental study has shown that high concentrations of Cr(VI) promote the formation of vaterite in a porous medium.[5]

OBJECTIVE

In this work, Raman spectroscopy analyses of crystal aggregates grown in a silica gel bearing a range of Cr(VI) concentrations were conducted. The morphology of these aggregates was consistent with that of vaterite. Our aims were (1) to find possible discrepancies between mineral identifications based on the spectroscopic analysis and on morphological criteria and (2) to propose plausible explanations for such discrepancies.

MATERIALS AND METHODS

A double diffusion system[6,7] consisting of two vertical branches separated by a column of silica hydrogel was used to crystallize calcium carbonate (Fig. 1). The vertical branches were filled with 0.5 M $CaCl_2$ and 0.5 M Na_2CO_3 solution, and different amounts of a Na_2CrO_4 solution were added to the silica gel during its preparation (0.1, 0.15, and 0.2 M). Crystals of the three polymorphs calcite, aragonite, and vaterite were recovered from the gel after 30 days. Vaterite aggregates were handpicked and studied by scanning electron microscopy and Raman spectroscopy. Experiments without chromate were also carried out. Although the formation of aggregates whose morphology matched that of vaterite was also observed in the absence of Cr(VI), these aggregates dissolved within a week of their formation and, consequently, could not be recovered from the gel.

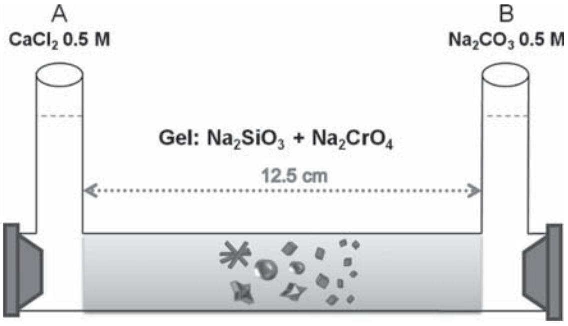

FIGURE 1 Schematic representation of the experimental system. The gel column was 125 mm long and 9 mm in diameter. The gel was prepared by adding 1 N HCl to a sodium silicate solution (Na_2SiO_3) (Merck KGaA, sp. gr.: 1.509 g/cm^3; pH = 11.2) until pH = 5.5 was reached. Different amounts of a Na_2CrO_4 solution were added to the mixture during the preparation of the gel.

Raman spectroscopy was conducted on a confocal Raman microscope (WITec alpha 300 R) employing a SHG Nd:YAG laser (532 nm, maximal power = 22.5 mW) for excitation and a lens-based spectrometer on the detection side (600 mm^{-1} diffraction grating; nominal resolution = 3.5 cm^{-1}). We observed the Stokes shift by rejecting the elastically scattered photons by a long pass filter. Spectra were recorded at 5 mW laser power with an integration time of 1 and 5 s with 10-fold averaging using a 100× microscope objective (working distance = 0.26 mm, NA 0.90).

RESULTS

Figure 2 shows examples of vaterite aggregates grown in the silica gel bearing 0.15 M and 0.20 M Na_2CrO_4, where their characteristic spherulitic morphology can be observed.

The Raman spectra collected from those aggregates that formed in gels containing $\geq$0.15 M Na_2CrO_4 show the typical vaterite triplet at 1074, 1081, and

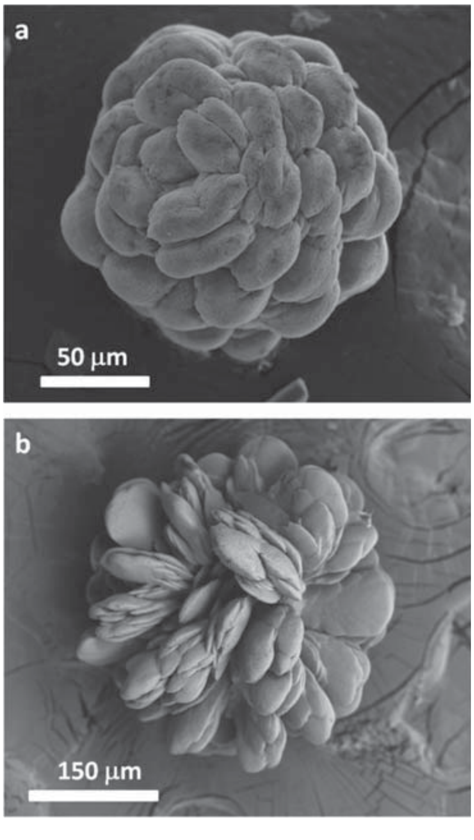

FIGURE 2 SEM micrographs of aggregates extracted from experiments with (a) 0.15 M and (b) 0.20 M chromate concentration.

1090 cm^{-1} corresponding to the $\nu 1$ vibration (symmetric stretching mode of the carbonate ion; Fig. 3A) due to the symmetric stretching mode vibration of the carbonate ion (Fig. 3A). The spectra are also well differentiated from calcite by their translational and rotational lattice mode vibrations between 100 and 300 cm^{-1} (Fig. 3B) and the vibrations in the region 600–750 cm^{-1} that correspond to internal translational modes of in-plane bending $\nu 4$ of the carbonate ions[8] (Fig. 3C). Table 1 summarizes the Raman vibrations obtained for the vaterite grown in the presence of 0.20 M of chromate.

Figure 3D shows some additional weak peaks in the region between 800 and 1000 cm^{-1} of the vaterite spectra (825, 838, 858, and 972 cm^{-1}). Those bands cannot be assigned to vaterite or any other $CaCO_3$ polymorph. However, according to several authors, they can be assigned to the Cr-O stretching vibration related to the presence of Cr in the vaterite structure.[5,9–11]

Figure 4A shows the SEM micrograph of a crystal obtained in the experiments conducted with low chromate concentrations (0.10 M). The Raman spectrum of this aggregate is depicted in Fig. 4B. As can be seen, in contrast to its external morphology, which is consistent with vaterite, its Raman spectrum shows peaks at 156, 282, 711, and 1085 cm^{-1}, which are all characteristic for calcite.[12] A closer examination of this sample (see the inset of Fig. 4A) shows that it consists of very small rhombohedron-shaped calcite crystals, that is, it is a calcite pseudomorph after vaterite.

TABLE 1 Raman Vibrations Obtained for Vaterite and Calcite

Substance	Lattice Modes (cm^{-1})	$\nu 1$ (cm^{-1})	$\nu 4$ (cm^{-1})
Vaterite	124, 153, 174, 213, 268, 301, 332	1074, 1081, 1090	665, 683, 709, 738, 751
Calcite	156, 282	1085	711

DISCUSSION

As has been mentioned above, aggregates showing the typical morphology of vaterite formed in all the experiments, including those carried out in the absence of Cr(VI). However, when the concentration of Cr(VI) in the growth medium was lower than 0.15 M, these aggregates either dissolved or

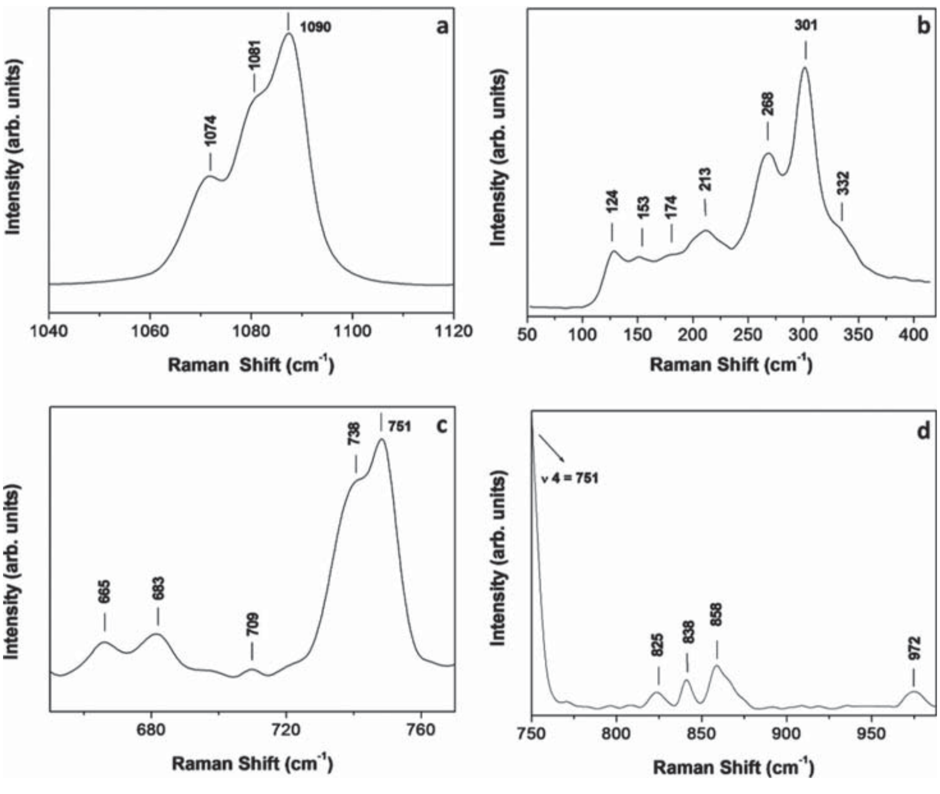

FIGURE 3 (a) Carbonate anion symmetric stretching bands ($\nu 1$). (b) Lattice modes. (c) Carbonate anion asymmetric bending ($\nu 4$). (d) Chromate bands.

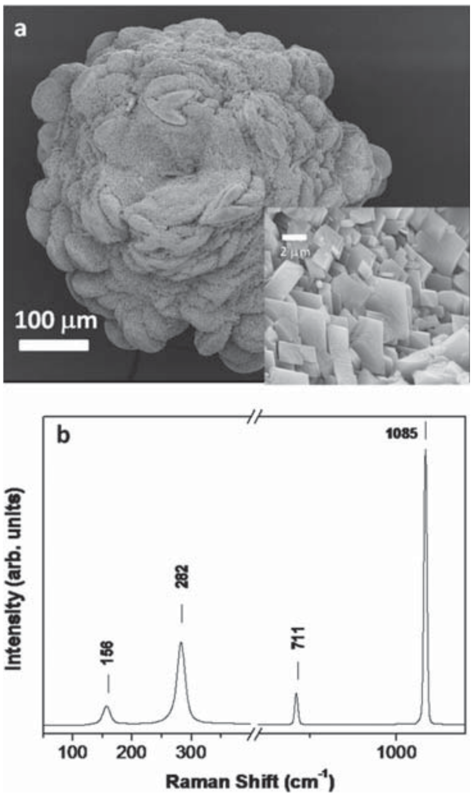

FIGURE 4 (a) SEM micrograph of the aggregate obtained in the experiments with 0.10 M of chromate in the gel. (b) Raman spectrum of the aggregate shown in (a).

transformed into calcite. Because this transformation occurred at 25°C, solid state diffusion can be considered negligible as a transformation mechanism. The transformation had to proceed via a vaterite dissolution–calcite precipitation process and can be described as a polymorphic solvent mediated transformation.[13] The metastable crystallization of vaterite can be explained by kinetic effects due to the high supersaturation under which crystallization in gels typically occurs. However, the fact that the transformation of vaterite into calcite is prevented when the Cr(VI) concentration in the growth medium is high cannot be explained exclusively considering kinetic factors. In fact, this result indicates that the driving force for the transformation of vaterite into calcite decreases as the Cr(VI) content in the growth medium increases. The driving force for this transformation directly relates to the solubility difference between vaterite and calcite. Since the Raman spectroscopy analyses indicate that vaterite grown in the presence of Cr(VI)-bearing solutions incorporates Cr(VI) into its structure, it can be concluded that Cr(VI)-bearing vaterite has solubility closer to that of calcite than pure vaterite or vaterite containing a very low amount of Cr(VI). In other words, as vaterite incorporates more Cr(VI), the driving force for the vaterite-calcite transformation decreases, and this transformation becomes less probable. A similar evolution of the solubility of sulfate-bearing vaterite has been proposed to explain the stabilization of vaterite with respect to calcite precipitated from aqueous solutions with increasing concentrations of sulfate anions.[4]

The preservation of the original shape of the vaterite aggregate after its transformation into calcite implies that this transformation has the characteristics of a mineral replacement process. This process is characterized by an interface coupling between vaterite dissolution and calcite precipitation.[14–17] The scale of the pseudomorphism (around 10 μm) indicates that this coupling was almost perfect, with vaterite dissolving and calcite precipitating at very similar rates.[18]

Our results show that the pseudomorphic replacement of vaterite by calcite easily occurs in porous media. This is relevant because the morphology of calcite crystals is often considered a genetic indicator. Spherical or globular calcites are interpreted as of biotic origin. For example, the finding of calcite globules in Martian meteorite ALH84001 in 1996 sparked an intense debate on their origin.[19] Since strictly inorganic vaterite tends to grow as spherical aggregates or as globules, our observation of the transformation of this phase into calcite in a short time with preservation of the external shape stresses the difficulty of drawing conclusions on the origin of carbonate phases exclusively on the basis of crystal morphology and mineral identification.[20]

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