

# Exploring Crystal Growth Dynamics of Calcium Carbonate and Phosphate in Silica Gels: Effects of Phosphate Concentration on Morphology and Composition

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## INTRODUCTION

Calcium carbonate and phosphate crystallization processes are fundamental in both geological and biomineralization contexts (Kuczumow et al., 2022a). This study explores the formation and characteristics of calcium carbonate and phosphate phases grown within a silica hydrogel medium, with particular focus on understanding the effects of phosphate ion concentration on crystal morphology and composition. Utilizing a U-tube setup, the diffusion of calcium chloride and sodium carbonate solutions through a silica gel matrix doped with potassium phosphate allowed the crystallization processes to be controlled, mimicking environmental conditions that may influence biomineralization and industrial applications.

## METHODOLOGY

A double diffusion system with silica hydrogel served as a medium for crystallization. Solutions of 0.5 M  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  were placed in the system, and experiments with and without added phosphate (50 and 500 ppm  $\text{Na}_3\text{PO}_4$ ) were conducted (Table 1). Crystal growth was observed at intervals of 15 and 30 days. Analytical methods included scanning electron microscopy (SEM), electron microprobe analysis (EMPA), and Raman spectroscopy to assess the morphological and compositional properties of the resulting crystals.

Mixture	Reagents		GEL	Tw <sup>1</sup>	Morphologies
	[CaCl <sub>2</sub> ]	[Na <sub>2</sub> CO <sub>3</sub> ]	[Na <sub>2</sub> PO <sub>4</sub> ]		
I	0.5 M	0.5 M	-	216 h	Rhombohedral Flower-like Radial
II	0.5 M	0.5 M	50 ppm	216 h	Elongated
III	0.5 M	0.5 M	500 ppm	168 h	Spheres
				360 h	Elongated

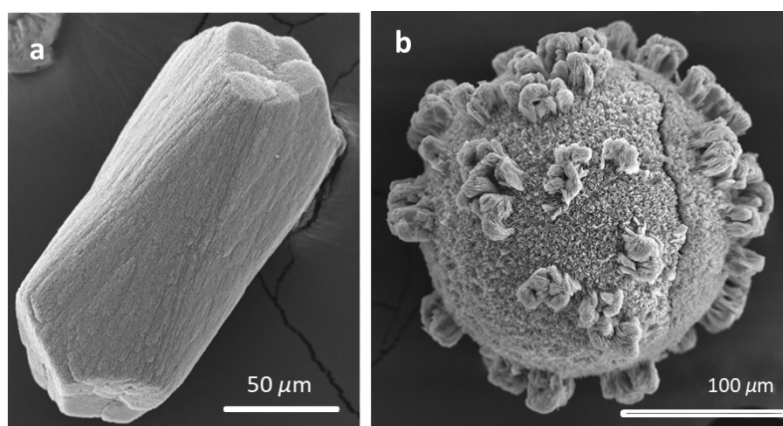
*Table 1. Concentrations of the solutions used in the gel experiments.*

## RESULTS AND DISCUSSION

The crystallization experiments in silica gel demonstrated that the presence or absence of phosphate in the medium significantly impacts the morphology and structure of the formed calcium carbonate and calcium phosphate crystals. In the phosphate-free experiment, scanning electron microscopy (SEM) and Raman spectroscopy revealed three distinct calcium carbonate morphologies: rhombohedral calcite crystals, flower-like vaterite aggregates, and spherical

aragonite forms. Calcite, the most abundant phase, displayed a typical rhombohedral shape with rough, centrally depressed hopper-like faces. These structures reflect the stable conditions of silica gel, which allowed for gradual ion diffusion and the formation of metastable phases, such as vaterite and aragonite, alongside stable calcite.

With the introduction of phosphate, even at low concentrations (50 ppm), a notable change in calcium carbonate morphology was observed. Calcite crystals adopted an elongated shape, dominated by the acute {0221} rhombohedron, with a morphology distinct from that of phosphate-free crystals (Figure 1a). This change is attributed to phosphate incorporation into the calcite structure, stabilizing specific faces and promoting the growth of elongated crystals. These findings align with previous studies showing that the presence of foreign ions in the crystallization medium alters calcite's habit through the preferential adsorption and incorporation of these ions on specific crystal faces (Titiloye et al., 1993; Davis et al., 2004). At higher phosphate concentrations (500 ppm), calcium phosphate crystal morphology evolved further, forming spherical aggregates with complex, multi-layered internal textures (Figure 1b). These aggregates exhibited characteristics similar to CO<sub>3</sub>-bearing OCP and HAP-like phases commonly observed in biomineralization. Raman analysis of these aggregates revealed peaks associated with PO<sub>4</sub><sup>3-</sup> and CO<sub>3</sub><sup>2-</sup> vibrations, suggesting the coexistence of calcium carbonate and phosphate phases within the same crystals. This type of sequential heterogeneous nucleation may reflect a process similar to bioapatite formation, in which carbonate and phosphate ions are incorporated in a controlled manner (Kuczumow et al., 2022b), imparting the material with its distinctive structural and mechanical properties.



**Fig. 1.** (a) Elongated calcite crystals. (b) Spherical aggregates showing the complex layered with different habits and morphologies.

These findings suggest that phosphate addition not only affects calcium carbonate morphology but also facilitates the formation of mixed calcium carbonate-phosphate phases, especially under high concentration conditions. This phenomenon of co-nucleation and crystal growth in silica gels has implications for understanding how complex, ion-rich environments, similar to biological conditions, can influence mineral crystallization and composition. The results underscore the importance of phosphate concentration in phase formation and habit modulation, providing valuable insights for biomedical and environmental applications, including bio-inspired material design and biomineralization processes.

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