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Migrating triplet precipitation bands of calcium phosphates in gelatinous matrix

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Outside the realm of biology and geology, one of the most beautiful and familiar examples of self-organized precipitate structure formation in nature can be found in reaction-diffusion systems. Though the patterned precipitations in reaction-diffusion systems was discovered by Raphael Eduard Liesegang more than a century ago [1], the mechanism of this nonlinear phenomenon is not yet fully understood and hence are still under discussion [2–5].

The formation of the banded precipitate patterns is due to the diffusion of an electrolyte A into a gelatinous matrix impregnated with another electrolyte B and the subsequent chemical reaction in a diffusion limited way [6]. Scientists speculated on the regular Liesegang banding framed three generic spatio temporal relations. The first one, called 'time law' connects the distance x_n of the nth band measured from the junction point of the two electrolytes and the time t_n of its formation through the relation $x_n^2 = \alpha\, t_n$. This result given by Morse and Pierce [7] reflects the diffusive behavior of the outer electrolyte into the gelatinous matrix. The second one, the 'spacing law' of Jablczynski [8] is a more intricate property of the bands, according to which the ratio between the positions of the adjacent bands follow a geometric series $x_{n+1} = \beta\, x_n$, where β approaches a constant value when the order of the rings is sufficiently large. The spacing between the bands $(x_{n+1} - x_n)$ normally increases as n increases. Hence the constant β referred to as the spacing coefficient is usually greater than unity and is generally expressed as $(1 + p)$ where $0.05 \leq p \leq 0.4$ [9]. Finally the width w_n of the nth band has observed to increase with n and obey the simple linear relation $w_n = \gamma\, x_n$ where γ is another constant [10].

The authors have recently developed a new model for the band formation [11–16] based on the assumption that the boundary which separates the outer ions and inner electrolyte migrate virtually into the positive direction of the advancement of the A type ions. Once the moving boundary concept is introduced, we found that the theory straight away upholds the time law, spacing law [11] and width law [16] in a more efficacious manner. With the assumptions and approximations of the model, we have obtained modified versions of the conventional laws as

$$\xi_n^2 = \alpha' \tau_n \tag{1}$$

$$\xi_{n+1} = \beta' \xi_n \tag{2}$$

$$w_n = F(c)\xi_n \tag{3}$$

where $\xi_n = (x_n - x_{n-1})$ is the spacing between the nth and the $(n-1)$th bands, τ_n is the time taken for the appearance of the nth band after the $(n-1)$th band is formed and α' is a constant. The term $\beta' = (1 + p')$ is the new spacing coefficient and $F(c)$ is the concentration function depending on the initial concentrations a_0 and b_0 of the reacting species [16].

While performing experiments on the crystallization of calcium phosphates in silica gel, Cartwright, Garcia-Ruiz and Villacampa [17] observed two competing crystal phases, hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] and dicalcium phosphate dihydrate [$CaHPO_4{\cdot}2H_2O$], such that they form two sets of Liesegang bands. Later Villacampa and Garcia-Ruiz [18] performed a series of experiments in silica gel for pH values ranging from 6.86 to 9.85. They have observed that by increasing pH values the system favors the formation of hydroxyapatite. Above 9.85 they obtained a homogeneous precipitate of hydroxyapatite alone [18].

This letter is a report of the work carried out by the authors to precipitate the multiple phases of calcium phosphates simultaneously into Liesegang bands in silica gel. Surprisingly, we have obtained dynamic triplet precipitate patterns inside the gel column at a pH below 6.86. The article addresses all the relevant aspects of the triplet patterns of calcium phosphates observed in silica gel matrix.

The experiments were performed in long glass tubes of internal diameter 6 mm, containing a vertical column of sodium meta silicate gel uniformly charged with ortho-phosphoric acid (H_3PO_4). Measured volume of $CaCl_2$ solution was poured over the gel as the source of cations. All the reactants used were AR grade. For pH

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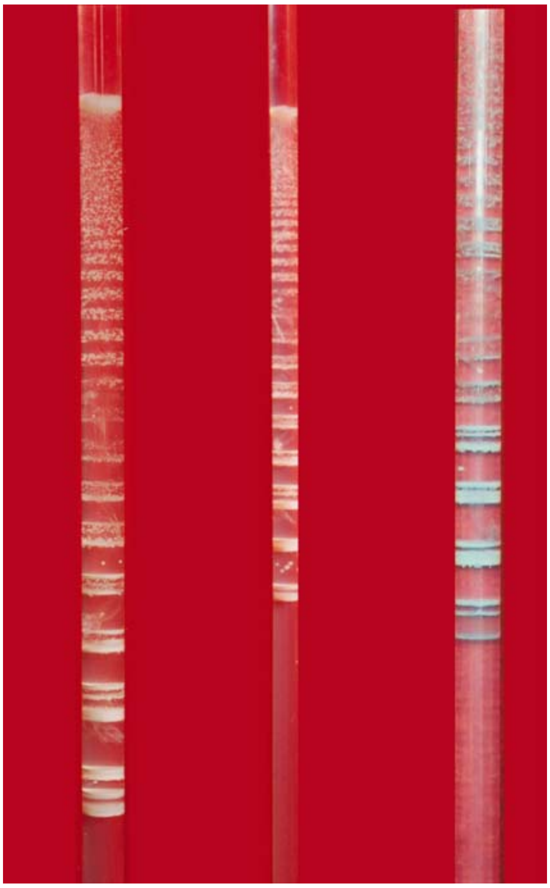

Figure 1 Triplet Liesegang patterns of crystallizing calcium phosphates. Experimental details: silica gel density 1.03 g cm^{-3}, pH 6 and 6.5, Outer electrolyte—$CaCl_2$ solution: 1.2 M, Inner electrolyte—H_3PO_4: 1.2 M.

values 6 and 6.5, three distinct sets of well-defined periodic bands in the form of microcrystals co-precipitate within a few days (Fig. 1). Another remarkable aspect observed in the system was the slow dissolution of the top bands and the subsequent formation of crystallites from the spherulites. By virtue of band formation at the bottom and band dissolution at the top, the whole stratum seems to migrate slowly down the tube. Nearly 20 triplet band structures were observed in the tubes in four months time of diffusion. During dissolution it is seen that the middle band of the triplet pattern dissolves first, followed by the other two.

In the crystallizing gelatinous medium the possible cationic species present are PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$. When Ca^{2+} diffuses into the medium, it may get react with these species resulting in the precipitation of respective compounds. The reaction kinetics of Ca^{2+} ions with the cations present in the system is different due to their charge density variations. The PO_4^{3-} species react immediately while the other two species HPO_4^{2-} and $H_2PO_4^-$ carrying less charge react slowly [19]. It is well known that on the basis of pH, solubility and Ca/P ratio, at least four different calcium phosphate phases can precipitate viz., hydroxyapatite — HAP [$Ca_{10}(PO_4)_6(OH)_2$], tricalcium phosphate—TCP [$Ca_3(PO_4)_2$], octacalcium phosphate — OCP [$Ca_8H_2(PO_4)_6 \cdot 5H_2O$], and dicalcium phosphate dihydrate—DCPD [$CaHPO_4 \cdot 2H_2O$] [19–21]. Among these, DCPD and HAP are thermodynamically stable compounds at ambient temperatures. Since both are slowly crystallizing substances, the other two (TCP and OCP) are often initial products and may tend to persist [19, 22].

TABLE I Estimation of the new spacing coefficient for the different species of calcium phosphate precipitates

pH	Type of species	ξ_{n+1}/ξ_n (individual bands)	ξ_{n+1}/ξ_n (triplet)
6	DCPD	1.1063	1.1208
	TCP-OCP	1.1183	
	HAP	1.1287	
6.5	DCPD	1.1094	1.1239
	TCP-OCP	1.1201	
	HAP	1.1334	

Nancollas [20], who extensively studied the precipitation of phosphates, plotting solubility isotherm as a function of pH using thermodynamic data, showed that for pH values between 6 and 7 the TCP and OCP phases are inseparable. Looking at the molecular mass and Ca/P ratio of the precipitate one can easily conclude that in the triplets observed the lowest band may be HAP, the middle one TCP-OCP combine and the upper one DCPD.

The apparent propagation of the pattern can be explained as follows. The reaction of $H_2PO_4^-$ with calcium ions produces unstable dicalcium phosphate—DCP [$CaHPO_4$] along with the liberation of hydrogen ions. This will lower the pH of the surrounding region. At low pH, the calcium phosphate precipitates are not stable. This may be a possible justification for the dissolution of the earlier formed bands [20]. The middle band of the triplet, the TCP-OCP combine, dissolves first as it is less stable than the other two.

The new spacing coefficient $\xi_{n+1}/\xi_n = (1 + p')$ is calculated for each set of bands by measuring the separation between them. It is seen that all the bands in the triplet were in precise geometric series and satisfies the spacing law (Table I). Also the triplet itself behaves as a system obeying the geometric law. It is also verified that the spacing coefficient depends on the pH of the medium. Extensive studies on the three different bands observed are in progress.

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