1. Introduction

Chemical gardens are the plant-like structures produced by a variety of different metal-ion salts when immersed in a solution of one or a number of anions, most investigated of which is silicate.$^1$ When the crystal of the salt begins to dissolve in the silicate, it reacts and forms a gel around itself. This gel acts as a semipermeable membrane, inhibiting the outflow of ions from the salt but permitting water from the silicate solution to flow in towards the salt crystal, driven by osmotic pressure. As the water flows and the crystal continues to dissolve, the pressure inside the membrane rises. At some point, in general, the membrane ruptures and a small hole is formed, through which the metal-ion solution inside flows out. This metal-ion solution reacts with the silicate outside; a tube around the flow growing by precipitation. The tube morphology is a product of the forced convection, driven by osmotic pressure, owing to the semipermeable membrane and free convection from buoyancy, since the ejected solution is generally lighter than the external silicate. The final result is a combination of tubes of different sizes and shapes, resembling a tree or a garden.

Although chemical gardens are by no means a newly discovered phenomenon,$^2$ this complex system, combining different physical processes with chemical reactions of dissolution, precipitation, nucleation, crystallization and polymerization, is not yet well-characterized in terms of understanding the physical and chemical parameters, in order to be able to control the morphology, composition and microstructure of these tubes.

The main interest in the chemical garden system has been for chemical demonstrations—which is somewhat ironic when the phenomenon is not yet fully understood—but it also has relevance to processes of industrial importance that involve precipitation across colloidal gel membranes separating two different aqueous solutions, for example the hydration of Portland cement$^3$ and the corrosion of metals.$^4$ It has also been proposed that the membranes of chemical gardens produced in submarine vents may be an ideal site for the origin of life.$^5$

While recent research has focused on controlling tube growth itself,$^6$ not much work has included a thorough study of their morphology, chemical composition and microstructure. Traube$^7$ hypothesized the formation of the semipermeable membrane, which was later experimentally confirmed by Pfeffer.$^8$ Coatman et al.$^9$ studied the morphologies and rate of growth at different silicate concentrations; Collins et al.$^{10}$ studied in detail the composition and structure of gardens grown from aluminium nitrate$^{10}$ and copper salts.$^{11}$ and Balköse et al.$^{12}$ used a wide variety of techniques to analyse the composition of gardens seeded with several metal-ion salts. Their formation mechanism and its relationship with microstructure and chemical composition is not yet well understood.

Thouvenel-Romans et al.$^{13}$ identified three different regimes of tube growth when injecting a copper sulfate solution into sodium silicate. At low concentrations of copper sulfate, they obtained thin silica tubes growing steadily in a regime they called “jetting”. At intermediate concentrations, the tubes grew wider and in a characteristic pulsating manner, in which a droplet periodically forms and detaches at the tip of the tube, a regime they called “popping”. At higher concentrations, they found a third regime, “budding”, in which the inflating droplet does not detach but instead bursts and nucleates a new droplet at the tube’s end. The resulting morphology is of wider, globular and twisted tubes.

The purpose of this article is to study the morphology and composition of tubes grown with alkaline salts using different sodium silicate concentrations. For a more systematic investigation, we centre the work on three cations of Group 2, Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$, which are especially interesting in the study of mineral formation and in the cement industry. The morphologies and microstructures were studied using ESEM, and compositional analysis was performed by EDX and XRD.
2. Materials and methods

To avoid initial conditions of different shapes, crystals of CaCl₂, BaCl₂ and SrCl₂ of analytical purity were generally homogenized with an agate mortar and pressed into 200 mg wafers of 1 cm diameter using a cell at a pressure of 10 bar over 10 min. This procedure permits a more uniform shape, and better control of the quantity and reactivity of these salts. In addition, in some cases indicated below, irregular grains were also used. Sodium silicate solutions were prepared from a commercial concentrated solution composed of 27% SiO₂ and 15% NaOH. They were diluted using twice-distilled water to several concentrations between 6 and 0.1 M. The growth process at room temperature was followed for at least 24 h, or as long as necessary for the salt to completely dissolve. The experiments were recorded using standard photographic equipment. Afterwards, the tubes were removed from the solution and dried in air at 25°C. Micrographs of the samples were obtained using a FEI Quanta 400 environmental scanning electron microscope (ESEM) operating at high vacuum and room temperature. Chemical analysis of the micromorphology observed by ESEM was performed in situ in the microscope using EDX analysis. Powder X-ray diffraction (XRD) analyses were performed in a PANalytical X’Pert PRO diffractometer. Identification of the crystallographic phases in the diffractograms was performed using the Xpowder program.14

3. Results and discussion

3.1 Calcium chloride

Initially, we studied the growth process of silicate gardens from calcium chloride under different conditions with sodium silicate solutions at several concentrations from 6 to 0.1 M. The reactivity and behaviour is dependent on the concentration of the silicate solution and the structure of the solid salt. After a short induction period, four kinds of behaviour of the CaCl₂ salt can be distinguished: (i) the formation of a transparent bubble as osmosis occurs, which we have named an “osmotic envelope”; (ii) the growth of wide transparent tubes with irregular globular forms from the osmotic envelope; (iii) the growth of narrow white tubes from the osmotic envelope or from transparent tubes; and (iv) the formation of a spongy mass.

The reactivity is much higher for salts in an irregular grain form than in a compressed wafer form. Obviously, in the former, the reactive surface is much larger; the surface irregularity increases the dissolution rate in the grain compared to that in the wafer.

In Fig. 1, we see the effect of different silicate concentrations on grains of CaCl₂. At high silicate concentrations (6 and 3 M, with densities $\rho = 1.39$ and 1.20 g cm⁻³, respectively¹•), a large transparent osmotic envelope is formed during the dissolution of the salt. The internal pressure coming from the osmotic flow produces the expansion of the spherical osmotic envelope by a self-renewal process of the membrane under the influence of the internal pressure. When the osmotic envelope growth is almost finished, some close-ended fingers grow in all directions (Fig. 1a). This growth regime seems to be diffusion-controlled, and dominated by plastic deformation and the elasticity of the membrane. The fingers are not more likely to grow upwards and the osmotic forces are more important than the forces of buoyancy, fingers developing from a Laplacian instability. These fingers, about 1–2 mm in diameter, are easily observable when we remove the solvent (Fig. 1b). When occasionally an air bubble appears on the tip of one finger, the buoyancy of this air bubble facilitates the upwards growth of this finger in a 1 mm-wide transparent tube in a popping growth regime (see the central tube in Fig. 1a). The strength and elasticity of the membrane inhibits the rupture of the osmotic envelope, and sometimes when the salt is completely dissolved and the osmotic envelope is accidentally detached from the reactor bottom, the buoyancy forces push up the whole osmotic envelope to the top. We can estimate a concentration of calcium chloride of about 12% in the internal solution, corresponding to a density of 1.10 g cm⁻³, which is lower than the density of the external solution ($\rho = 1.39$ g cm⁻³). The transparency of the osmotic envelope, these fingers and their tubes, as well as their flexibility and elasticity, may be due to their extreme thinness and colloidal nature.

With a lower concentration of silicate, around 1 M ($\rho = 1.06$ g cm⁻³), the salts grow a collection of white narrow tubes (Fig. 1d). No expansion of the spherical envelope is observed. The osmotic membrane formed with a lower silicate concentration is possibly thinner, meaning that it becomes broken in many places due to the buoyancy forces. The inner solution is expelled by a jetting growth regime, precipitating rapidly the silicate and forming the white tubes. Some intermediate behaviours are observed with silicate concentrations in the range 1–3 M, where the reactivity seems to reach a maximum, with shorter induction times and longer tube lengths than with higher and lower silicate concentrations.

![Fig. 1](https://example.com/fig1.png) Chemical gardens from calcium chloride grown at 6 M (a and b), 2 M (c), 1 M (d) and 0.3 M (e) sodium silicate solutions. All pictures are in solution, except b, which is without solvent. The picture size is approximately 2 cm wide.
concentrations. In the example in Fig. 1c with 2 M silicate, a central wide transparent tube is formed initially, and subsequently many white tubes grow out, breaching the membrane around them. At silicate concentrations below 1 M, the salt dissolves, forming a spongy mass, in which no spherical membrane is distinguished. Many white tubes grow out very slowly and lean against the container wall, as seen in Fig. 1e.

When using pressed wafers, the reactivity is drastically lower, but the experiments become more systematic and reproducible. The use of the wafer also helps to avoid salt hydration during its handling at ambient humidity. The general behaviour starts with the formation of a gel membrane around the wafer, which then becomes the transparent osmotic envelope with 3 M silicate, as seen in Fig. 2a–c. As the envelope inflates, it may trigger transparent fingers, wide transparent twisted tubes or narrow white tubes. Usually, the wider tubes grow first in periodic pulses at about 3 cm min\(^{-1}\) following a budding growth regime, often changing direction with every burst. The narrow, white tubes do not appear until the wider tubes have stopped growing or until some external excitation (vibrations, shaking) occurs and the membrane breaks.

We propose that the formation mechanism of the transparent tubes is different to that of the white ones. The transparent tubes are not produced by a rapid rupture of the membrane, but by an elongation of the same membrane, forming a finger and growing upwards owing to a combination of osmotic and buoyancy forces. This also explains the same transparency of the tube walls and bubble. The width of these tubes helps the slow and regular formation of the tube walls. When the osmotic and buoyancy forces are strong enough, the membrane of the finger tip stretches and breaks, concurrent with the formation of a new extension of the membrane with the flow of the inner solution. This extension of the walls increases the volume and the internal pressure is released. This produces a cessation of the flow, closing the tip of the tube. Again, the osmotic flow increases the inner pressure and the freshly formed membrane will become broken, following a random direction, and forming another segment of the membrane wall, as explained above. The budding growth tends to be periodic, yielding bulging but unbranched hollow tubes. These tubes will be more or less vertical, depending on the strength of the buoyancy forces.

The white narrow tubes can grow directly from the bubble or from the endings of wider tubes (Fig. 2b) and always in a rather vertical manner, indicating a greater influence of buoyancy forces, as opposed to the forced convection that produced the transparent tubes. After the formation of the spheroidal envelope and the transparent tubes, the concentration of calcium will be lower than in the initial solution, owing to the entrance of water and the quantity of calcium used in the membrane wall formation. Hence, the density difference between the internal and external solutions will be larger than in the initial situation, and so the buoyant forces will be larger. These forces will try to break the colloidal membrane at any inhomogeneity, and the inner solution will exit, forming the relatively straighter white tubes of about 0.2 mm in diameter in a jetting growth regime.\(^{19}\) The transparency difference between the two types of growth may be explained by their different thicknesses, and also by the different interstitial water content or colloidal state,\(^{16}\) which would also explain the flexibility of the transparent tubes versus the fragility and stiffness of the white ones.

The influence of gravity can be observed in the sequence shown in Fig. 3. In that case, a calcium chloride wafer is immersed in 3 M silicate in a 5 mm-wide Hele–Shaw cell. The salt does not develop a spherical bubble because of the restriction imposed by the walls, but it still forms a transparent bubble.

Fig. 2 Chemical gardens grown from calcium chloride wafers in 3 M (a–c) and 1 M (d) sodium silicate. Gardens (a) and (b) were grown in cylindrical flasks, producing transparent tubes first and white tubes later. The experiment in figure (c) was grown in a Hele–Shaw cell of 5 mm width. The picture size is approximately 2 cm wide by 5 cm tall.
membrane that permits us to see how the salt dissolves from top to bottom. The presence of gravity produces buoyancy forces between the different solutions and the salt wafer, which is still solid inside its osmotic envelope. The water that flows through the membrane is lighter than the inner metal-ion solution, which makes it accumulate above, dissolving the wafer from the top.

With a 1 M silicate solution and wafers, the osmotic envelope size is much smaller than with 3 M, and only white narrow tubes are formed (Fig. 2d). As seen previously, the membrane formed with 1 M silicate breaks in many places and many jets of inner solution move upwards, forming the white tubes. These tubes do not grow alone, but rather as a cluster of many microtubes. The membrane is probably broken in many sites close to each other, and this facilitates the formation of the disordered cluster of tubes. However, the origin of the different morphology of these white tubes with respect with the transparent tubes is not yet well understood. Further experiments are necessary for us to understand this phenomenon properly.

In Fig. 4a,b, we show ESEM images of a typical transparent tube after it has been dried. We can see how the surface textures are clearly different for the internal and the external sides of the tubes: smooth on the outside and rough on the inside. The elasticity is highly dependent on the water content, which is lost during drying, producing many cracks on the surface (Fig. 4b). An EDX analysis indicates that the outer surface is mainly non-crystalline polymerized silica with calcium sodium silicate. The rough inner surface is composed mainly of calcium oxide, with the presence of CaCl₂ micro-grains in the lower growth zone (Fig. 4c) and NaCl in the upper. The narrow, white tubes form clusters of microtubes (Fig. 4d), with multilayer walls (Fig. 4e) and thicker external walls (>10 μm after drying) than the former transparent tubes (<1 μm after drying). Their composition is mainly calcium silicate on the outside, shifting towards calcium oxide on the inside. The Ca²⁺ cations of the inner solution flowing out from the membrane react with the silicate of the external solution and precipitate a calcium silicate layer. During ageing, SiO₂ units of the external solution are deposited on the external surface of these tubes, increasing the chemical content of silicon in this layer. The interactions of the internal face of this tube wall with the Ca²⁺ cations solvated by the basic medium (H₂O + OH⁻) enhance the precipitation of calcium oxide/hydroxide on the internal face of these walls, increasing the chemical content of calcium and oxygen with respect to silicon. This phenomenon occurs in all tubes of any morphology.

In some cases after long reaction times, an amount of calcium carbonate is detected, particularly in the upper segments, probably due to a small amount of carbonate in the medium from atmospheric CO₂ and owing to the low solubility of this carbonate in the high pH of the solution. However, this carbonate does not participate in the formation of chemical gardens and is only an artifact due to impurities.

### 3.2 Strontium and barium chloride

Sr²⁺ and Ba²⁺ salts were studied exclusively using wafers. In both cases, the reactivity is lower than in the Ca²⁺ case under similar conditions, both in the induction time, and in the formation of the osmotic envelope and tubes. While with calcium chloride the tubes grew steadily to a length of several centimetres, with strontium or barium salts, the tubes grow to
regions are the original SrCl₂, but the darker ones are made of undissolved salt inside. Analyzing the remains of the wafer by osmotic envelope from the silicate while it still contained some microspheres of NaCl, proving that the sodium cation may cross the semipermeable membrane. We also separated a piece of the osmotic envelope and imaged it using a backscattered electron detector, the brightest areas correspond to the initial SrCl₂ (brightest areas). This indicates that the only highly crystalline phases in these silicate gardens are NaCl and carbonates. The main phases are mostly silica and silicates in an amorphous or disordered state, which is well known in the formation of calcium silicate in Portland cements, where reverse chemical gardens are produced during the hydration of cements, forming a mesh of microtubes that fill the inter-grain spaces and a cohesive matrix that is responsible for the strength of the paste. The formation of NaCl occurs mainly in the inner surface of the membrane and tubes, and this is clear evidence that the Na⁺ cations cross the osmotic membrane and form halite crystals with the chloride anion of the seed. The crystallization of carbonates is owing to their low solubility at the basic pH of the silicate solutions and to the presence of CO₂ in the atmosphere absorbed by the silicate solutions. The formation of carbonates is more likely to be observed in the strontium and barium cases owing to their lower solubility. Some small needles of carbonates are observed by ESEM-EDX in the outer surface of the upper part of some white tubes in the calcium (Fig. 7a) and barium (Fig. 7b) cases. The precipitation of these carbonates is not visible in the X-ray analysis, as shown in Fig. 6d,e. However, the EDX analysis of the outer surface shows that the precipitation is different to that of the external surfaces.

### 3.3 X-ray analysis

In order to perform X-ray powder diffraction of the chemical gardens, the tubes were separated from the rest of the sample to explore differences in the crystallinity and chemical composition between the various morphologies of different parts of the chemical gardens. Calcium tubes did not show a high crystallinity, except for NaCl crystals, whose reflection peaks were the most intense and the only ones clearly observed at 27.8, 31.8, 45.4 and 56.5° (2θ values). Barium and strontium tubes, however, showed clear reflection peaks belonging to carbonates. In the barium spectrum, the peaks at 24.06, 34.18, 42.17 and 44.86° (2θ values) belong to BaCO₃; there also being observed reflection peaks of NaCl. In the strontium spectrum, the peaks at 29.68, 36.46 and 47.71° (2θ values) belong to SrCO₃, while those at 12.90, 22.38, 25.23, 33.91 and 40.97° belong to undissolved SrCl₂·6H₂O; peaks of NaCl are also observed. Barium and strontium carbonate peaks were the most intense and the only ones clearly observed in the X-ray analysis of the chemical gardens, the tubes were separated from the rest of the sample to explore differences in the crystallinity and chemical composition between the various morphologies of different parts of the chemical gardens. Calcium tubes did not show a high crystallinity, except for NaCl crystals, whose reflection peaks were the most intense and the only ones clearly observed at 27.8, 31.8, 45.4 and 56.5° (2θ values). Barium and strontium tubes, however, showed clear reflection peaks belonging to carbonates. In the barium spectrum, the peaks at 24.06, 34.18, 42.17 and 44.86° (2θ values) belong to BaCO₃; there also being observed reflection peaks of NaCl. In the strontium spectrum, the peaks at 29.68, 36.46 and 47.71° (2θ values) belong to SrCO₃, while those at 12.90, 22.38, 25.23, 33.91 and 40.97° belong to undissolved SrCl₂·6H₂O; peaks of NaCl are also observed. This indicates that the only highly crystalline phases in these silicate gardens are NaCl and carbonates. The main phases are mostly silica and silicates in an amorphous or disordered state, which is well known in the formation of calcium silicate in Portland cements, where reverse chemical gardens are produced during the hydration of cements, forming a mesh of microtubes that fill the inter-grain spaces and a cohesive matrix that is responsible for the strength of the paste. The formation of NaCl occurs mainly in the inner surface of the membrane and tubes, and this is clear evidence that the Na⁺ cations cross the osmotic membrane and form halite crystals with the chloride anion of the seed. The crystallization of carbonates is owing to their low solubility at the basic pH of the silicate solutions and to the presence of CO₂ in the atmosphere absorbed by the silicate solutions. The formation of carbonates is more likely to be observed in the strontium and barium cases owing to their lower solubility. Some small needles of carbonates are observed by ESEM-EDX in the outer surface of the upper part of some white tubes in the calcium and barium cases. The precipitation of these carbonates is not visible in the X-ray analysis, as shown in Fig. 6d,e. However, the EDX analysis of the outer surface shows that the precipitation is different to that of the external surfaces.
of carbonates is an artifact coming from impurities and does not come from the formation of chemical gardens.

4. Conclusions

We found CaCl₂ to be more reactive than the other salts of Group 2 in terms of tube length, diameter and growth speed. Calcium tends to produce long, wide and flexible tubes, while strontium and barium produce short, narrow tubes that sometimes grow as clusters. The strontium salt is slightly more reactive than the barium one. This is consistent with the sequence of the relative solubility of these salts: CaCl₂ > SrCl₂ > BaCl₂. The chemical hardness of Ca²⁺ is the highest of the alkaline earth cation series studied in this work, and it tends to form M₂-[(OH⁻)]₂ complexes more easily than the rest of the cations. The optimal concentration for the sodium silicate solution in chemical garden growth with these salts is around 3 M, in good agreement with the findings of Coatman et al.; higher and lower concentrations tend to reduce the reactivity. The concentration of the solution affects the shape and rate of formation of the tubes, in part presumably through its viscosity. With a higher viscosity (higher silicate concentration), the reaction is slower and the viscosity of the external solution allows only a few slow-growing tubes to emerge. At the other extreme, very dilute concentrations fail to produce a coherent colloidal membrane, and the precipitated material forms a spongy mass. The reason is that at higher concentrations, the thickness and elasticity of the membrane is great enough to allow it to expand and inflate without breaking. On the other hand, at lower concentrations with less silicate in the solution, the membrane formed bursts sooner, ejecting the internal solution promptly and forming multiple white tubes instead of maintaining or expanding the transparent membrane.

Electron microscope imaging showed that the tube walls are not homogeneous across their section; there is both a morphological and a compositional difference between the inner and outer surfaces. Analysis of the different morphologies indicates that the tubes are formed by two separate layers, metal oxide on the inside and metal silicate on the outside. This happens for all the alkaline earth cations studied in this work. However, separation between the layers is not clear and EDX analysis does not have enough resolution to verify this discontinuity. The kinetics of the fast precipitation of tube wall formation probably does not allow the formation of a clear interface, especially in the formation of white narrow tubes.

X-Ray diffraction showed the tubes to have a low crystallinity while amorphous components hide the highly ordered phases. Nevertheless, the highest crystallinity phase comes from the
formation of NaCl. The presence of NaCl crystals in the inner surface of the tubes indicates that the Na\(^+\) ions can cross the semipermeable membrane.

In some cases, we observed pulsating growth of wide transparent tubes, producing irregular morphologies that were clearly influenced by the thickness and mechanical properties of the membrane. When the membrane first breaks, a jet of the internal solution flows out. The contact of this flow with the external solution produces the precipitation of the silicate of the Group 2 cation, forming the walls of the tube. As the flow of the metal-ion solution loses its initial injection pressure, the precipitation of silicate closes the tip of the tube, interrupting its growth. The osmotic membrane will then need some time to regain enough transparency. This behaviour is only seen in the wider tubes as elongations of the same membrane, preserving the same morphology and thickness.

Fine control of the fluid dynamics, the relative densities between the different solutions and the osmotic pressure could provide tools to engineer microtubes with a desired morphology and thickness.

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