

A Tungstate Chemical Garden

Carlos Pimentel,^{*,[a, b]} Jlyan H. E. Cartwright,^[a, c] and C. Ignacio Sainz-Díaz^[a]

Tungstate chemical gardens have been prepared for the first time. The synthesis was carried out using cobalt(II) chloride and sodium tungstate. The reaction occurred in three steps: chimney formation, swelling, and upwelling of the chemical garden. This result opens the door to a new variety of materials.

Chemical gardens are fascinating self-organizing inorganic structures consisting mainly of tubes and vesicles, which biomimic plant-like structures. From a first description by Johann Glauber in 1646,^[1] chemical gardens have attracted attention. In the last few years, scientists have been interested in chemical gardens to explore a wide variety of scientific questions. This research field has been recently called chemobionics.^[2] There is a great variety of subjects that can be studied through chemobionics, e.g., corrosion, electrochemistry, sensors, and chemical motors.^[2,3] One of the most interesting scientific questions in the ambit of chemobionics is the origin of life, since life could have originated in oceanic hydrothermal vents, which are natural chemical gardens.^[2,4-8]

Experiments to promote the formation of classical chemical gardens consist in adding to a solution of an anion a metal salt (all except the too-soluble alkali metals), in solid form of single crystals or as polycrystalline powder compressed into a pellet, or alternatively as a second liquid. A number of different solutions and metals have been shown to lead to the growth of chemical gardens.^[2] In the solution, the commonest anion used is silicate, but many other anions have been also used: e.g., carbonate, phosphate, borate, arsenate and chromate.^[2] Metals used to precipitate chemical gardens have been, e.g., Ca, Mg, Co, Ba, Fe, Cu and Zn, just to mention a few.^[2,9] Interestingly, the growth of chemical gardens using crystals of anions and solutions of cations have also been reported.^[2,10] These kinds of inverted systems have been described for polyoxometalates (POMs).^[9] POMs are complexes with polyatomic ions, which can contain W, Mo, Mn, P, or Si in their structure.^[10,11]

However, to date, no work has been reported using single tungstate as the anion in classical chemical gardens. Tungstates are interesting compounds used as catalysts in organic chemistry (e.g., in the oxidation of alcohols into aldehydes or ketones or in the epoxidation of alkanes),^[12] especially in stereoselective epoxidation in the synthesis of the popular antibiotic, Fosfomycin.^[13] Cobalt tungstate (CoWO₄), in particular, has proved to have a number of industrial applications, making it a very interesting compound in economic terms. Some of those applications are, e.g., photocatalytic materials for water oxidation,^[14] electrode material for supercapacitors^[15] or microwave dielectric ceramics.^[16] Furthermore, CoWO₄ appears in nature as a result of the burning of coal mine dumps. This phase is known as krasnoselskite, although it is not recognized as a mineral by the IMA. In this paper, we demonstrate for the first time the formation of tungstate chemical gardens, based on cobalt tungstate.

The growth of tungstate chemical gardens was carried out using a cobalt chloride pellet and sodium tungstate solution. CoCl₂·6H₂O analytical grade powder was ground in an agate mortar to homogenize the solid. 40 mg of ground CoCl₂ was pressed using a cell at 2 tonnes over 5 min to obtain pellets of 5 mm diameter and 1 mm thickness. Na₂WO₄·2H₂O analytical grade powder and Milli-Q membrane-purified water were used to prepare a 1 M sodium tungstate solution with an initial pH of 9.7. The experiments were carried out at room temperature.

The pellet was placed at the bottom of a 5 ml glass flask. Approximately 4.5 ml of the tungstate solution were slowly added down the side of the flask. After a few seconds, two fuchsia colour chimneys grew vertically (marked by white arrows in Figure 1). These tubes were accompanied by the formation of some sharp platy side precipitates. A couple of minutes later, the pellet started to swell up from liquid entering from the external solution through a semipermeable membrane formed around the pellet, growing a balloon-like structure with pink colour. The lower part continued to swell up, acquiring a rounded botryoidal shape with pink colour. Some fingering phenomena were also observed. During this swelling process, small air bubbles formed around the lower part of the chemical garden (Figure 1). This could indicate the formation of a gas phase during the tungstate – cobalt reaction. Such gas phase has not been identified yet. Nevertheless, these gas bubbles have been observed also in previous chemical garden formation.^[17] They come probably from the air trapped in the pellet. When the formation of the osmotic balloon is very fast these gas bubbles remain trapped attached to the external surface of the solid structures formed in the chemical garden.

The chemical garden remained at the bottom of the flask for a few minutes, after which it detached from the base of the flask and rose up to the top of the external solution. The density

[a] C. Pimentel, J. H. E. Cartwright, C. I. Sainz-Díaz
Instituto Andaluz de Ciencias de la Tierra
CSIC – Universidad de Granada
18100 Armilla, Granada (Spain)
E-mail: c.pimentel@csic.es

[b] C. Pimentel
Departamento de mineralogía y petrología
Facultad de Ciencias Geológicas
Universidad Complutense de Madrid, 18040, Madrid (Spain)

[c] J. H. E. Cartwright
Instituto Carlos I de Física Teórica y Computacional
Universidad de Granada, 18071 Granada (Spain)

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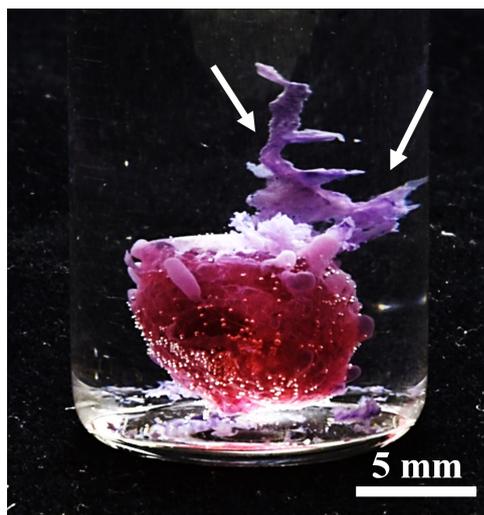


Figure 1. Tungstate chemical garden with a botryoidal-rounded shape and pink colour. Above it, two initial chimneys of a fuchsia colour can be seen, indicated by two white arrows. Underneath the chemical garden, a number of small air bubbles can be observed.

of the internal fluid is lower than that of the external fluid and buoyancy forces will have pushed up the balloon to the top surface on breaking its attachment to the reactor bottom. The small bubbles formed around the chemical garden remained after its rise to the top. This buoyancy also turned the chemical garden upside down, with the tubes being below the balloon (Figure 2). Note that the colour of the tubes is different to that of the balloon. The color change from pink to fuchsia indicates a change in the types of ligands around the Co^{2+} cation where some of the water molecules have changed by O atoms joined to the tungstate group.



Figure 2. Tungstate chemical garden after the upwelling process. At the top of the flask the rounded botryoidal shaped element can be observed, and, below it, the two chimneys, indicated with two white arrows. In the flask bottom, a tiny ridge can be observed, indicated by a yellow arrow.

The cobalt cation Co^{2+} can react with the tungstate anion forming layers as in the structure of the tungstate mineral wolframite, $(\text{Fe},\text{Mn})\text{WO}_4$. We took the experimental crystal structure^[18] and performed an isomorphous cation substitution of Mn^{2+} cations by Co^{2+} . Quantum mechanical calculations based on density functional theory (DFT) were performed on this system. DFT was used to optimize the crystal structure of CoWO_4 crystals applying periodical boundary conditions. All electronic calculations were performed with CASTEP code including in the Material Studio package.^[19] Generalized Gradient Approximation (GGA) functional with the PBE parameterization were used. Ultrasoft pseudopotentials and an energy cutoff of 571.4 eV were applied. These conditions have proved to be satisfactory in previous calculations of periodical systems of other minerals.^[20] Open-shell calculations were performed allowing the spin polarization. Formal spins were used as initial spin for each atom, i.e., 3 for Co, 2 for W and 0 for O. The convergence gradient for the self-consistent field (SCF) for energy calculations was 1×10^{-6} eV/atom in the density matrix. Convergence tolerance parameters were set in 1×10^{-5} eV/atom for energy, 0.03 eV/Å for maximum force, 0.05 GPa for maximum stress and 0.001 Å for maximum displacement.

After full optimization (atomic positions and cell lattice parameters) the crystal structure of cobalt tungstate was reproduced ($a=4.65$, $b=5.61$, $c=5.0$ Å; and $\alpha=90^\circ$, $\beta=90.9^\circ$, $\gamma=90^\circ$; and space group $P2_1/c$) in accord with the experimental values ($a=4.67$, $b=5.69$, $c=4.95$ Å; $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$; and space group $P2_1/c$).^[21] The slightly lower value of the a axis of cobalt tungstate has also been observed experimentally in other tungstate minerals, like sanmartinite, where the cation is Zn.^[22]

Observing the detail of the crystal structure of cobalt tungstate, both transition metals, Co and W, have an octahedral coordination. Applying the radial distribution function in this optimized structure, we calculated the average bond lengths between transition metals and oxygen atoms being similar, 2.01 Å for Co–O and 1.99 Å for W–O. A layered stacking is observed in the relative positions of the cations (Figure 3). The internal fluid enriched in Co^{2+} cations reacts with the tungstate anion from the external fluid precipitating and forming the tube walls.

In conclusion, in this study, we have demonstrated the formation and growth of tungstate chemical gardens. In particular, we report here the growth of a cobalt tungstate chemical garden, which shows three different growth stages: i) chimney formation, ii) swelling, and iii) upwelling. During the swelling process, the osmotic membrane forms a great balloon, which eventually leads to the upwelling of the chemical garden turning upside down. This surprising result opens the door to perform further research into the optimization of experimental parameters for the formation of these structures and a subsequently deeper characterization of these materials.

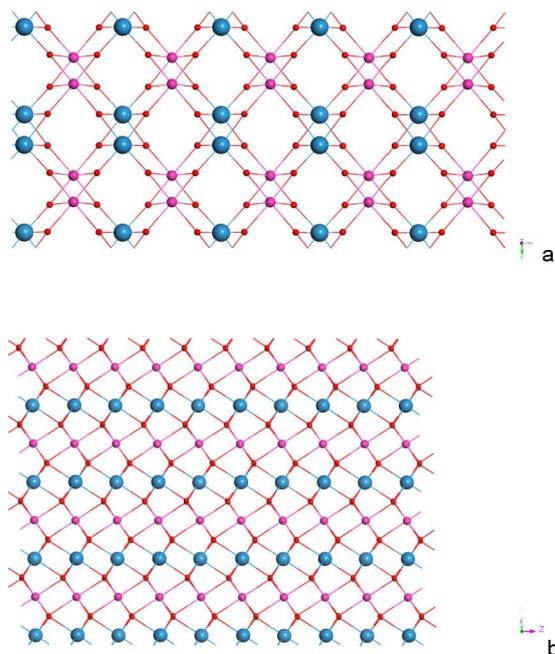


Figure 3. Optimized crystal structure of cobalt tungstate seen from the 001 (a) and 010 (b) planes. The O, W, and Co atoms are shown in red, blue, and pink, respectively.

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Conflict of Interest

The authors declare no conflict of interest.

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