Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

## Silica gardens without silica: The formation of pure metal hydroxide tubes

Bruno C. Batista and Oliver Steinbock*

Department of Chemistry and Biochemistry, Florida State University,

Tallahassee, FL 32306-4390, USA

**Summary:**

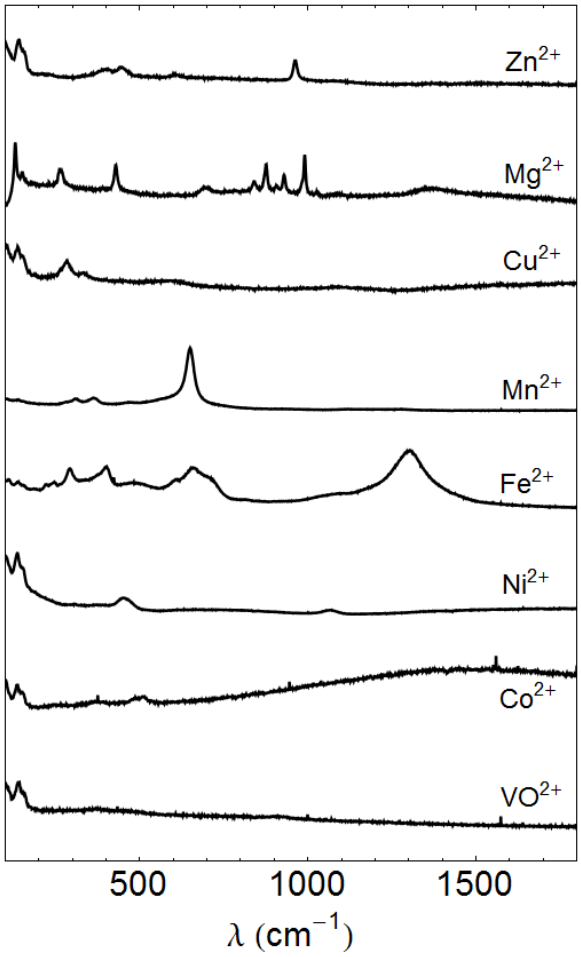


Figure S1. Raman spectra of silica-free precipitation tubes. Equal amounts of material were collected from tubes grown at a pump rate of 8 mL/h. The concentration of $OH^-$ and the divalent cations was 0.5 mol/L. Raman spectra were collected using a Jobin Yvon Horiba LabRam high-resolution spectrometer coupled to an optical microscope (50× objective). The excitation wavelength was 633 nm for all specimens except Mg (785 nm). The power at the sample was 0.6 mW (633 nm) and 0.8 mW (785 nm), respectively. The signals were normalized to the same maximum intensity.

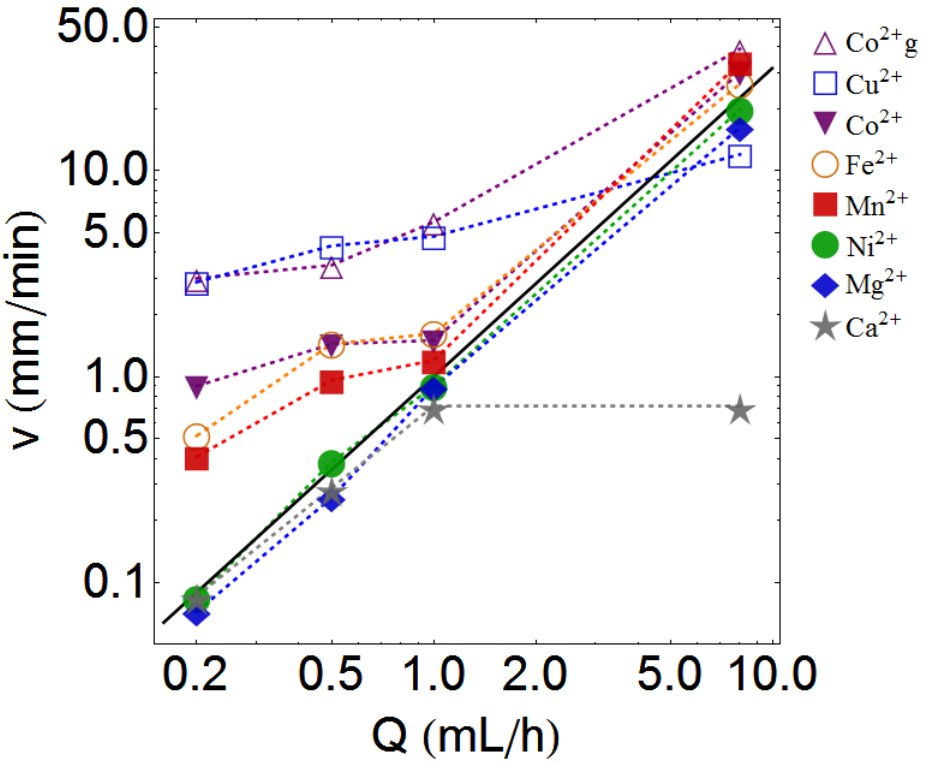


Figure S2. Double-logarithmic plots of the tubes' growth speed *v* as a function of the employed pump rate *Q* for our full set of results. The marker symbols distinguish between different metal chloride solutions (all 0.5 mol/L; see legend); dotted lines are only meant as a visual guide. The continuous black line has a slope of 3/2. Open triangles represent an experiment where glucose (0.5 mol/L) was added to a solution containing $Co^{2+}$ ions.

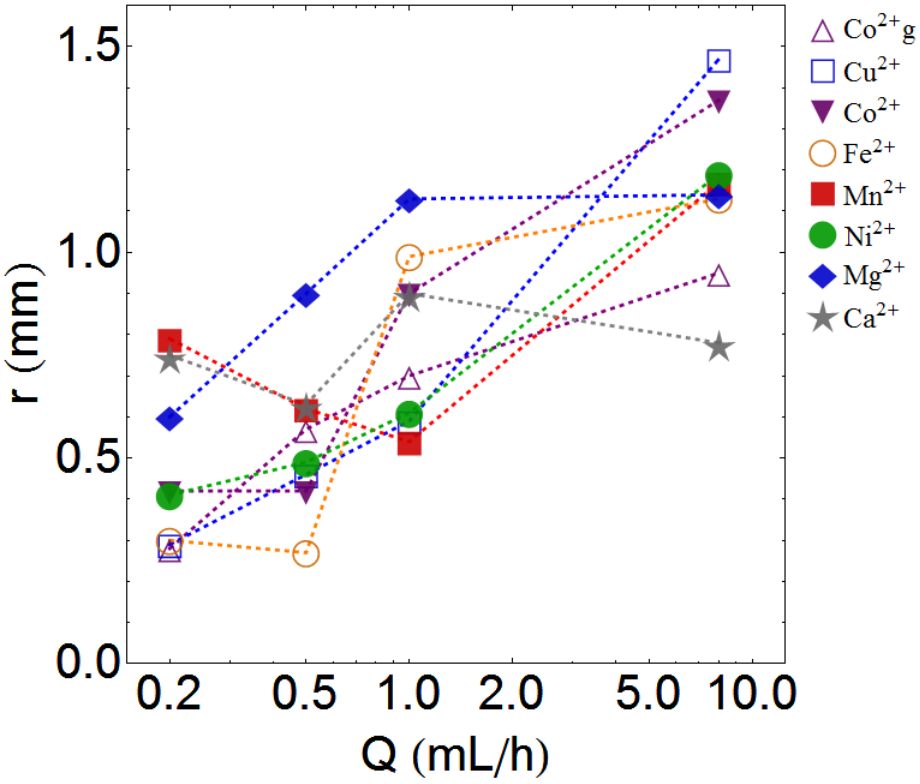


Figure S3. Half-logarithmic plots of the tubes' radii *r* as a function of the employed pump rate *Q* for our full set of results. The marker symbols distinguish between different metal chloride solutions (all 0.5 mol/L; see legend); dotted lines are only meant as a visual guide. Open triangles represent an experiment where glucose (0.5 mol/L) was added to a solution containing $Co^{2+}$ ions.

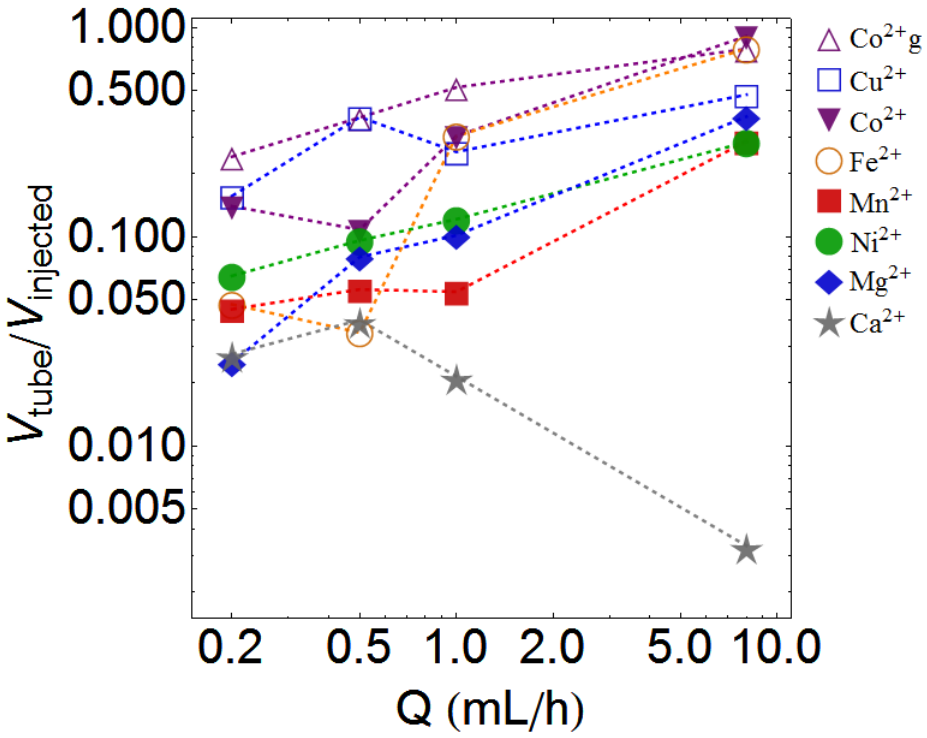


Figure S4. Double-logarithmic plots of the ratio between the approximate tubes' volume $V_{tube}$ and the amount of metal salt solution injected $V_{injected}$, as a function of the employed pump rate $Q$ for our full set of results. The marker symbols distinguish between different metal chloride solutions (all 0.5 mol/L; see legend); dotted lines are only meant as a visual guide. Open triangles represent an experiment where glucose (0.5 mol/L) was added to a solution containing $Co^{2+}$ ions.

**Table S1 – Physicochemical properties of solutions and tubes' growth velocities**

| | *Density (g/mL)* | *pH* | *-log($K_{SP}$) for Hydroxide* | *v (mm/min) at 0.2 mL/h ± 10%* | *v (mm/min) at 0.5 mL/h ± 10%* | *v (mm/min) at 1 mL/h ± 10%* | *v (mm/min) at 8 mL/h ± 30%* |
|---|---|---|---|---|---|---|---|
| *$MgCl_2$* | 1.034 | 4.8 | 13.2 | 0.072 | 0.26 | 0.89 | 16.2 |
| *$CaCl_2$* | 1.04 | 5.1 | 5.3 | 0.086 | 0.29 | 0.72 | 0.72 |
| *$MnCl_2$* | 1.048 | 4.8 | 11.2 | 0.41 | 0.96 | 1.2 | 33.6 |
| *$FeCl_2$* | 1.05 | 2.7 | 16.3 | 0.52 | 1.44 | 1.62 | 26.4 |
| *$CoCl_2$* | 1.052 | 4.4 | 14.2 | 0.9 | 1.4 | 1.5 | 30 |
| *$NiCl_2$* | 1.054 | 5.5 | 15.2 | 0.084 | 0.38 | 0.9 | 19.8 |
| *$CuCl_2$* | 1.057 | 3.0 | 19.6 | 2.9 | 4.3 | 4.8 | 12 |
| *$CoCl_2$ (gluc)* | 1.086 | 4.2 | 14.2 | 3 | 3.48 | 5.64 | 39 |
| *$ZnSO_4$* | 1.078 | 5.8 | 15.5 | - | - | - | - |
| *$VOSO_4$* | 1.056 | 1.2 | - | - | - | - | - |
| *NaOH* | 1.019 | 13.4 | - | - | - | - | - |

Table S1. Tube growth velocities at four different flow rates and the corresponding pH values and densities of the original reactant solutions. The table is complemented by the solubilities of the respective metal hydroxides. The latter data is taken from [1,2].


1 W. M. Haynes, T. J. Bruno, D. R. Lide, *CRC Handbook of Chemistry and Physics 96th Edition*, CRC Press, Boca Raton, **2015**.

2 P. Patnaik, *Handbook of Inorganic Chemicals*, McGraw-Hill, New York, **2002**.

## Table S2 – Position of Raman peaks ($cm^{-1}$)

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Zn** | 140 | 398 | 445 | 601 | 961 | 1078 | | | | | | |
| **Mg** | 128 | 150 | 264 | 428 | 694 | 839 | 875 | 909 | 928 | 991 | 1027 | 1355 |
| **Cu** | 137 | 282 | 334 | 595 | 1099 | | | | | | | |
| **Mn** | 308 | 362 | 649 | | | | | | | | | |
| **Fe** | 136 | 218 | 245 | 291 | 400 | 482 | 604 | 656 | 1084 | 1301 | | |
| **Ni** | 136 | 450 | 1064 | | | | | | | | | |
| **Co** | 252 | 373 | 496 | 1484 | | | | | | | | |
| **VO** | 140 | 386 | 912 | | | | | | | | | |

## Table S3 – Position of XRD peaks (2θ in degrees)

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Zn** | 11.7 | 12 | 12.4 | 13.6 | 17 | 21.4 | 23.4 | 24.5 | 26.5 | 27.1 | 31.9 | 33 |
| | 33.5 | 34.4 | 35 | 36.3 | 37.6 | 40.8 | 41.2 | 41.7 | 43.6 | 44.6 | 45.4 | 47.7 |
| | 49 | 50 | 51.7 | 56.6 | 58.8 | 59.2 | 60.2 | 61.2 | 62.9 | 64.2 | 67.9 | 69 |
| | 70.3 | 70.9 | 72.5 | 74 | | | | | | | | |
| **Mg** | 18.8 | 33.2 | 38.2 | 51 | 58.9 | 62.2 | 68.4 | 72.2 | | | | |
| **Cu** | 16.6 | 23.7 | 34 | 35.6 | 38.6 | 39.6 | 43.4 | 48.8 | 53.2 | 57.7 | 61.4 | 63 |
| | 65.8 | 67.9 | 71.9 | 73.4 | | | | | | | | |
| **Mn** | 18.2 | 29.2 | 31.3 | 32.6 | 36.4 | 38.3 | 44.7 | 50.1 | 51 | 54.2 | 56.2 | 58.8 |
| | 60.1 | 64.9 | 67.9 | 69.9 | 74.4 | | | | | | | |
| **Fe** | 18.1 | 21.3 | 26.8 | 30.3 | 33.4 | 34.9 | 35.7 | 36.8 | 40.2 | 41.3 | 43.3 | 47.3 |
| | 53.4 | 57.3 | 59.1 | 61.4 | 62.9 | 64.1 | | | | | | |
| **Ni** | 11.3 | 14.5 | 21.1 | 33.6 | 39.2 | 59.6 | 72.6 | | | | | |
| **Co** | 11.2 | 19.3 | 22.5 | 33.8 | 38.2 | 51.8 | 59.3 | | | | | |
| **Vo** | 19.4 | 36.2 | 50.5 | | | | | | | | | |

**Note S1 – Description of SI movies.**

**SI Movie 1**. Fountain-like colloidal particles are observed during the injection of a NaOH solution into a vessel containing $CaCl_2$. The concentration of both reactants is 0.5 mol/L. The movie is speeded up by a factor of five and each frame corresponds to $3 \times 5.8$ cm$^2$. Note the gradual growth of a white CaOH tube above the point of injection. The pump rate is 8 mL/h.

**SI Movie 2**. Oscillatory cycles of tube precipitation and dissolution during the injection of a NaOH solution into a vessel containing $VOSO_4$. The concentration of both reactants is 0.5 mol/L. The movie is speeded up by a factor of five and each frame corresponds to $3 \times 5.8$ cm$^2$. The pump rate is 1 mL/h.